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PUSA







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SERIES A

CONTAINING PAPERS OF A MATHEMATICAL AND  
PHYSICAL CHARACTER.

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# PROCEEDINGS OF THE ROYAL SOCIETY.

## *SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCES.*

### *Address of the President, Sir Charles Sherrington, O.M., at the Anniversary Meeting, November 30, 1925.*

Let me in the first place refer, even if briefly, to those whom death in the past year has removed from the roll of the Fellowship. The losses this year have been numerous. I follow the order of their occurrence.

GEORGE DOWNING LIVEING, chemist, who held the Chair in Cambridge from, if we include the term of his deputy tenure, 1859 until 1908, and witnessed his University pass, largely owing to his own influence, from a stage with hardly any provision for the practical teaching of chemistry to a development of it such as pertains to the full modern scale of requirement. His original contributions to his science lay largely in spectroscopy. Part of his personality was a vigour, bodily and mental, retained into advanced age, for he had reached his 98th year. He had been throughout his career a force in his University. He was awarded the Davy Medal in 1901.

WILLIAM WHITAKER, geologist, and in the service of the Geological Survey for 39 years. He continued to render unofficial help to the Geological Survey almost up to the extreme end of his long life of 88 years.

WILLIAM MITCHESON HASWELL, zoologist, Professor of Biology in the University of Sydney. An untiring investigator in the field of comparative anatomy; his varied work included the description of a number of remarkable animal forms which he was the first to record. His latest paper, published only last December, amplified a monograph on the Temnocephalæ that he had published thirty years before. He was joint author with Geoffrey Parker of a large text-book of zoology, of standard reference throughout the English-speaking world.

JAMES MACKENZIE, physician, specially distinguished for the advances he made in, and the impetus he gave to, modern clinical study of diseases of the heart, work begun and largely completed amid the pre-occupations of a general

medical practice at Burnley. There he devised his polygraph for recording simultaneously the arterial and venous pulses to gauge the action of the heart's auricle, a key to the understanding of disturbed rhythm of the heart. In 1907 he came to London and devoted himself to consultant work with great success. Finally, he removed to St. Andrews, where his name will always be connected with the Institute for clinical study which he there founded.

OLIVER HEAVISIDE, mathematical physicist. Withdrawing in early life from business as a telegraph engineer, he devoted himself in retirement to problems of electricity and of its applications. It has been written of him that he, perhaps more than any other one man, proved the value of mathematical theory to the electrical industry. He was elected a Fellow of the Society in 1891. Two years later appeared the first volume of his 'Electro-Magnetic Theory'; the third and concluding one in 1912. He described what is now familiar to the radio engineer as the Heaviside layer, by which, it is supposed, Hertzian waves are bent round the earth. He was a nephew of Charles Wheatstone.

HORACE TABBERER BROWN, chemist and botanist. Largely self-taught in natural science, though having received some formal instruction in chemistry, he entered a brewery, and at once recognized the scope for microscopic and chemical study of yeasts, and of the then novel cognate studies of Pasteur on Vinous Fermentation. It has been penetratively remarked that he achieved for brewing improvement and success analogous to those achieved for surgery by Lister. He further contributed fundamental researches on the transformation and shift of the reserve carbo-hydrate in germinating grain; also on changes in the green leaf during photosynthesis, and on the amount of absorption of carbon dioxide through the stomata in relation to gaseous diffusion. He received a Royal Medal in 1903 and the Copley Medal in 1920.

EDWIN KLEIN, histologist and bacteriologist, for many years a teacher in the Medical School of St. Bartholomew's Hospital, and an investigator, mainly bacteriological, for the Medical Department of the Local Government Board. He had been a Fellow of the Society for close on 50 years.

THOMAS CLIFFORD ALLBUTT, physician, Regius Professor of Physic at Cambridge from 1902 until his death, in his 89th year. By character and attainments, an outstanding figure in Medicine throughout his long career. Of Yorkshire family, the first 27 years of his professional life were spent in Leeds, and in that period he helped to bring into general clinical use

the sphygmomanometer for measuring blood pressure; and he introduced the clinical thermometer in its present practical form. At Cambridge, he was not only the titular head, but the life and soul of the Medical School. He did much public work for the organization of Medical education throughout the country. He was made a Privy Councillor in 1920. An accomplished writer, there can hardly be a more charming example of him as such than the obituary notice of his old friend Pridgin Teale, which he furnished for the Proceedings of this Society two years ago. He was a Vice-President of the Society from 1914 to 1916.

EDWARD THORPE, chemist, distinguished in research, in teaching and in administration. His accurate measurements of specific volumes of liquids of related chemical constitution, led him to conclusions which at the time were novel. His researches with Dr. Tutton into the oxides of phosphorus brought among other results the discovery of the tetroxide, also incidentally the recognition of the oxide ( $P_4O_6$ ) as the cause of the jaw-necrosis of match-factory workers, a recognition which enabled the stamping-out of the disease. The atomic weight of radium was the subject of his Bakerian Lecture in 1907. He will be remembered also in connection with the Magnetic Survey of the British Isles. Professor of Chemistry at Leeds, and then at South Kensington, and then Government Chemist, he returned to South Kensington as Professor of General Chemistry in the Imperial College of Science and Technology, and retired at the end of the war. He was foreign Secretary of the Society from 1899 to 1903.

JOHN CLELAND, anatomist, at first of Queen's College, Galway, and then for 32 years in the Chair of Anatomy at Glasgow. His original contributions were of considerable volume, but his chief impression upon his time was as a teacher.

GEORGE NATHANIEL CURZON, Marquess Curzon of Kedleston, elected to the Society under Statute 12 in 1898, had travelled extensively in Asia. Was Viceroy and Governor-General of India from 1899 to 1905. A great public servant in many successive capacities.

ARTHUR DENDY, zoologist. He completed for the Challenger Reports the memoir on the monaxonid sponges. At one time Lecturer in Melbourne University and then Professor in Canterbury College, New Zealand, he contributed notable observations on a number of Australasian forms. Work on the pineal eye, the discovery of the ciliated grooves below the brain in the New Zealand lampreys, and a paper on the Reisner fibre of the central nervous system of Vertebrates, are items among his output of work. He was busy

with the silicious sponges when his fatal illness overtook him. He had held the Chair of Zoology in King's College, London, for 19 years.

ALBIN HALLER, chemist, foreign member. From pharmaceutical training he had, as is not infrequent in France, passed to a career in pure chemistry. He made an exhaustive study of camphor and its condensation products with aldehydes and ketones. He furnished an important series of papers on the synthesis of anthracene derivatives. He introduced the idea that the alcohols can act on esters in the presence of hydrogen chloride in the same way that water acts. He was an ardent worker for the cause of technical education, and, largely owing to his efforts, the Chemical Institute was formed at Nancy. For twenty-five years he was Professor of Organic Chemistry at the Sorbonne.

WILLIAM FLETCHER BARRETT had held the Chair of Physics in the Royal College of Science, Dublin, from 1873 to 1910. He made contributions of original value to physics, but devoted his science mainly to the cause of teaching.

FELIX KLEIN, mathematician, foreign member, an eminent geometer and an untiring contributor to almost every branch of mathematics. He will be remembered also as an editor of the "*Annalen der Mathematik*," and as an originator of the *Encyklopädie of Mathematics and Mathematical Physics*, to which he gave long and devoted service.

GEORGE DASHWOOD TAUBMAN GOLDIE, an authority on West African, and especially on Nigerian, questions; he was elected a Fellow under Statute 12 in 1902.

FRANK EVERS BEDDARD, zoologist, and for more than thirty years Prosector to the Zoological Society. His special studies lay in the Oligochæta, and his well-known monograph on that natural order contains some of his best work.

FRANCIS ERNEST JAPP, chemist. His researches dealt especially with certain of the diketones, and belonged mainly to the years when he was Assistant Professor at the College of Science at South Kensington. He later held the Chair of Chemistry at the University of Aberdeen for 24 years.

FRANCIS DARWIN, botanist, whose botanical work included much research, especially into the transpiration and the movements of plants. He was associated with the botanical work of his father, Charles Darwin, and he wrote of him the biography, the well-known "*Life and Letters*," by common consent one of the most admirable and delightful accounts ever written of a great scientific life, the modesty and simplicity of the presentation contributing to its charm. He was awarded the Darwin Medal in 1912. He served as Foreign Secretary of the Society from 1903 to 1907, and was a Vice-President in 1917 and 1918.

EDWIN HENRY BARTON, physicist, Professor in the University College of Nottingham, his birthplace. He was the author of numerous original papers dealing with magnetism, electric waves and with acoustics. He was elected a Fellow in 1916.

WILLIAM SCHLICH, eminent in forestry both as an administrator and as a teacher. Twenty-four years of his earlier career were engaged in India under the Forests Department of that Government, and there he met continually increasing responsibilities with memorable success. He was then appointed to the staff of the Forestry Branch of the Royal Engineering College at Coopers Hill and subsequently to the Professorship of Forestry at Oxford, from which Chair he retired six years ago. Advanced age slackened but little his enthusiasm and industry, and up to the last he was revising for a new edition his 'Manual of Forestry,' the third revised volume appearing only this year.

JAMES SYKES GAMBLE, another eminent member of the Indian Forest Service. When he first went out to India in 1871, the botany of the Indian forest was for the practical forester's purposes imperfectly known, and the Indian timbers were hardly known at all. Early during his period of service he had furnished by his admirable 'Manual of Indian Timbers' a treatise which has been the standby of generations of Indian forest officers.

ANDREW GRAY, physicist, Professor of Natural Philosophy in the University of Glasgow, his *alma mater*, and where he had, during nine years of his earlier life, been assistant to Sir William Thomson (Lord Kelvin). He was author of a well-known treatise on 'Absolute Measurements in Electricity and Magnetism.'

JOHN YOUNG BUCHANAN, oceanographer. While with the "Challenger" expedition, he demonstrated the inorganic nature of the gelatinous deep-sea deposit which it had been suggested was a primitive living matter. His analysis of certain deep-sea deposits furnished the basis of John Murray's theory of the formation of coral-islands. In his later active life, he collaborated much in the oceanographical work of Prince Albert of Monaco, and in organising the Oceanographical Institute in Paris. Working, however, largely in private laboratories of his own, he accomplished much more than he ever published. His more important papers were issued in a volume from Cambridge, where he resided and was for a time Lecturer on Geography. A member of the scientific staff of the "Challenger" expedition, he had outlived all his fellow-members of it.

JOHN NEWPORT LANGLEY, a physiologist of unswerving reliability and fidelity

to research. His earlier work traced the relation between the granules of the living secreting cell and the amount and character of the gland's secretion. In 1889 he, in conjunction with his pupil Dickinson, communicated to this Society the observation that nicotine selectively paralyses the transmission of nervous impulses through the ganglia of the sympathetic system. Using this reaction as a main means he proceeded in collaboration with Dr. (now Sir) Hugh Anderson and others to unravel, in a completeness wholly remarkable, what had seemed the inextricable maze of the ganglionated nerve paths to viscera and skin. He showed that the principles underlying their anatomical and functional arrangement were of striking and unexpected simplicity. And this, with Gaskell's previous work, put the whole anatomy and physiology of the sympathetic system upon a new basis, opening it up for the further studies of to-day. Incidentally, during that work he showed that the property of double conduction, already recognized for nerve fibre, explains certain spreads of reaction, his axon reflexes. He succeeded Michael Foster in the Chair at Cambridge in 1903. As Editor of the *Journal of Physiology* he rendered long and arduous service. Of the marked renaissance in British physiology brought about in his time it may be said that he himself was one of the forces to whom that renaissance was due. He was awarded a Royal Medal in 1892, and was a Vice-President of the Society in 1904.

Turning now to other events of the year, on July 22nd the Society had the honour and pleasure of receiving a visit from Their Majesties the King and Queen. It afforded an opportunity for showing to the Royal visitors the exhibits prepared for the second annual soir  e, and a demonstration on Echo-Sounding for Navigational Purposes given by Mr. F. E. Smith. The Queen graciously added her signature to other Royal signatures in the Society's Charter-Book.

A dutiful address has but a few days since been sent to His Majesty expressing the deep sympathy of the Society in his bereavement by the death of the universally beloved Queen Alexandra.

The generous bequest of £10,000 received last year from an anonymous donor for the promotion of medical research has this year, on the recommendation of the Tropical Diseases Committee of the Society, been resorted to for prosecuting investigation into the disease kala-azar, endemic in India and the Orient. At the instance of the Society, Major Patton and Dr. Hindle started for Northern China in June last in pursuance of that object. And now, as you have seen from the Council's report, the Society has received from the same generous and anonymous source a further munificent bequest of some-

thing over £28,000, to be applied on the same terms and under the same condition of anonymity. Those directions will be observed with grateful remembrance.

This year the Society, at the request of the Government, has again organised, through a committee appointed for the purpose, an exhibition of pure science at the British Empire Exhibition. The catalogue of last year's exhibition was revised, enlarged and republished under the title 'Phases of Modern Science.' It is estimated that the Pure Science Exhibition has been visited this year by at least 120,000 persons. It has thus brought before a wide public the importance of scientific inquiry, pure and applied. Mr. F. E. Smith, the Chairman; Mr. Martin, the Secretary, and their colleagues of the committee, receive our thanks for an arduous effort and our congratulations on the success it has attained.

From the fund accruing to it in 1921 by the bequest of Miss Foulerton, the Society has this year been able, in pursuance of its scheme for advancing Natural Knowledge by the establishment of Research Professorships, to institute a further Foulerton Professorship, and the new Foulerton Professor appointed is Professor A. Vivian Hill. Professor Hill is already universally known as a most distinguished and fruitful investigator in animal physiology. His contributions in that field have been many and of outstanding importance. He has placed the knowledge of muscular contraction—if he will allow me that customary phrase, to which I believe he is purist enough to entertain some objection—upon a new footing. Taking up the problem from the viewpoint which chemical researches had at that time reached, Hill, by his own experiments and experiments in conjunction with his pupils and others, has carried its study much further, especially in its physical aspects. The technique devised and the lines of analysis pursued have been masterly. He has attained preciser measurements, both of the energy changes and of their time relations and of the mechanical work realisable. Examining under various conditions the several ratios existing between these quantities, he has thrown fresh light upon the intimate mechanism of muscle. Not always has it been entirely welcome news that Professor Hill has brought us about our muscles; we learn from him that they are sadly viscous machinery, but to that he reconciles us by pointing out compensatory advantages arising from that property. It is abundantly clear that the more the opportunity he has of prosecuting his inquiries, the more shall we and the world learn of the capacity and intricacies of bodily function. Deeper acquaintance with the principles underlying that function should enable better advantage to be taken of it. Some of Professor



Hill's results already touch practical issues of that kind. He is determining decisive factors concerned in the performance and maintenance of physical effort, and is tracing physiological characteristics underlying the skill and endurance of the athlete. Such researches promise information of value in regard to the management of muscular effort and its application on a whole-sale scale to industrial labour. They also promise further insight into what may be termed manual skill. Professor Hill's researches concern, therefore, questions of large practical as well as of theoretical importance. May his tenure of the Foulerton Research Professorship provide him with the amplest opportunity for cultivating the fertile field which has already conspicuously prospered under his able hands.

This Society is one of the oldest of scientific societies, and science grows rapidly, and change is a part of its growth. That the Society vitally participates in that growth and change is evidenced by the increasing stream of papers which pours in upon it. The Society, coexistent as it is in this its third century with many distinguished and flourishing special societies, can view with satisfaction such evidence that it in uncontracted degree supplies a needed channel for scientific issue of new work. The fact testifies that in harmony with its younger sister societies, it provides in unabated measure a living force for the scientific development of its time.

As regards the biological papers brought before the Society, one feature of the time which I think they impress upon the listener, is that at this present the growth of what one may term the experimental biological sciences—physiology, pathology, bacteriology, and pharmacology—is in some measure a convergent growth. Their individual boundaries seem more and more to merge. They are individual in their application rather than in their essential nature, and an advance made by one is of immediate advantage to all. Of any particular paper it would be often difficult, were it desirable, to say under which of these individual sciences it might best be singly classified or catalogued. Nor, under the elastic working of the Society, does that create difficulty; and that again, I think, affords evidence of the practical efficiency of our working arrangement.

With certain stages of growth there goes on the other hand increasing independence of an individual science. This seems so to-day for psychology viewed under the rubric of experimental biology. That psychology is rapidly growing is evident—not least so from its enhanced and successful application to practical problems lying before it in the sphere of industrial management and conditions of labour. Psychology as a part of experimental biology possesses,

\* of course, recognized ties with the physiology and pathology of the nervous system; but on them it no longer explicitly leans to the extent it did. Its discipline becomes more intrinsically its own. This is, to my mind, well, and of favourable augury for its immediate progress as an experimental science. Concurrently with that tendency in psychology it is noteworthy that physiologists, Professor Pavlov and his school, with in this country Dr. Anrep, are pursuing analyses of complex behaviour of the higher animals under systematic avoidance of all reference, even by implication, to such psychical reactions as accompany that behaviour. Their method applies to animal behaviour, in wider ambit than hitherto, the principles of reflex action. To illustrate by one example:—In his admirable Croonian Lecture in this room last June, Professor Magnus described analyses by himself and his colleagues of the pure reflex behaviour of the cat without cerebral hemispheres. He showed how, for example, a moving mouse before the eyes of such a cat attitudinizes the whole mechanism of the animal, exciting from it appropriate posture and direction in readiness for the final spring upon its prey. After that, “all the cat has to do is to decide to jump.” To jump or not to jump, that becomes the question. At such a point it is that the work of Pavlov and his school dovetails on to the work of Magnus and his school. Pavlov shows how in the intact animal such a final turning-point in its train of reactive behaviour—for instance, “jump” or “not-jump”—can be studied as what is termed a “conditioned reflex”; he shows how that turning-point can be examined as outcome of a balance between physiological impulsions and restraints, dependent partly on conditions under which the act is called for at the moment, partly on conditions under which it has been called for in the past—that is to say, the physiological history of the act in the individual, the mutual time-relations of the dominant stimuli, and so on. The result is thus treated as a sum of physiological factors, positive and negative, interacting under physiological rules, which can be determined, therefore, as obtaining for the cerebral cortex. In this way is pursued a physiological study of higher nervous functions of the animal brain, without appeal to psychical reactions, of which, indeed, the method affirms nothing and denies nothing. To my thinking this line of attack is a gain both for physiology and for psychology, since psychology and physiology, thus treading an essentially common terrain, yet do so each untrammelled by the other and without explicit reference to the eternal psychophysical problem.

But it would be a far step, and a difficult, and of questionable gain, to carry such divorce of psychology and physiology into the study of fields such, for

instance, as human speech, with what that connotes for reaction in the human brain. There it would seem better, as in Dr. Head's analysis of aphasia, to treat the anatomical, physiological and psychical data together. This seems the better, possibly the only, course of approach to those highest conjoint physiologico-psychological problems, than which there can be few scientific problems which are of greater or more special interest to man.

By reason of the completion of the statutory term of his office, to-day sees the retirement from the Biological Secretaryship of Sir William Hardy. His tenure included the greater part of the duration of the war, years of unusual difficulty in many ways. Throughout his period of office the Society has owed much to his ability and to his breadth of view. Perhaps not the least among his services have been the catholicity and level width of interest and sympathy he has given to biology throughout its entire range, and even beyond it, and to the field naturalist's side and to the laboratory side alike he has done signal service. I tender him, on behalf of the Society, and in the name of his fellow officers, grateful and hearty thanks.

And let me now—feeling that this meeting will, in accordance with precedent, view my so doing as no pre-election trespass—offer welcome to the distinguished biologist nominated to follow in the office of the Secretaryship. Also let me extend to the name, of unsurpassed eminence in science, nominated for our Presidency a welcome no less hearty. Every good wish to them both.

Before passing to the presentation of the medals, my last official act, let me offer my very hearty thanks to the Society, to the Members of Council with whom I have served, and to my fellow officers throughout the period of my office; also to the Assistant Secretary, Mr. Towle, and to the Assistant Librarian, Mr. White, and to all the members of the staff. My best thanks are due to them, and I tender them sincerely, for the goodwill, kindness and forbearance shown in such full measure to me. The office to which the Society did me the honour of electing me now five years ago I have, I need not say, esteemed as a very great honour; the kindness received on all hands during my endeavour to discharge its responsibilities leaves me its recollection as not only a high privilege but an ineffaceable pleasure.

The Copley Medal is awarded to Professor Albert Einstein.

The name of Einstein is known to everyone through the theory of Relativity which he originated in 1905 and extended by a notable generalization in 1915. Previous investigators had discovered that electromagnetic phenomena for a moving system could be correlated to a "local" or fictitious time and space-

reckoning, determined by the motion of the system. Einstein realised that the time and space with which we are so directly acquainted by experience can be no other than the fictitious *local* time and space of the moving system—the motion in this case being that of the earth; we have no means of determining, nor can physical science be concerned with, any absolute reckoning of space and time. It followed that the classical scheme of physics, erected on this terrestrial space-time framework, partakes largely of the geocentric standpoint supposed to have been abandoned from the time of Copernicus. Einstein opened our eyes to the existence of a broader standpoint from which the strange and complicated results of motion—such as the Fitzgerald contraction and the change of mass with velocity—were banished, as the earlier revolt from a geocentric view of nature had banished the complicated cycles and epicycles of Ptolemy. After this Einstein was led to the identification of mass with energy—another result of far-reaching importance, which allows us to know the exact amount of the store of energy so tantalizingly hidden within the atom.

There was a feeling that this theory of relativity for uniform motion must be a particular case of something more general; but observational knowledge seemed to oppose a decisive negative to any extension. It was Einstein again who found the way to the generalization of bringing gravitation into his scheme. Just as the complex phenomena of the moving system had been found to arise in the process of referring its description to an irrelevant frame of space and time, so the phenomenon of gravitation was found to arise in referring a non-Euclidean region of the world to an irrelevant Euclidean frame. At first sight this seems to be an abstract geometrization of a physical subject, substituting an appeal to pure geometry, instead of rational mechanical explanation. But the real effect has been rather to reduce natural geometry to a branch of physics; it is now recognized that the metre rod is a physical appliance for exploring the field of inertia and gravitation, as the magnetic needle explores the electro-magnetic field; and the results of the two kinds of exploration of the world ought not to be given differential treatment.

Einstein's general theory of relativity is remarkable alike for the brilliance of conception and the mastery of the mathematical implement required to develop it. The mathematical technique is now familiar to many, and the new thought has become almost commonplace; but we do not cease to marvel at the genius which first found the way through the overwhelming obstacles. The new law of gravitation must be reckoned the first fundamental advance in the subject since the time of Newton. It involves an interaction between gravitation and light, which had indeed been suspected by Newton and almost

taken for granted by Laplace, though it dropped out of scientific speculation when the corpuscular theory of light gave way to the undulatory theory. The three crucial astronomical tests of Einstein's theory have all been verified—the motion of perihelion of Mercury, the deflection of light, and the red-shift of the spectral lines. The last-named proved the most difficult to test, but there is now general agreement that it is present in the solar spectrum. More recently Einstein's theory of gravitation has appealed to astronomers not merely as something which they are asked to test, but as a direct aid to the advancement of astronomical research. The *tested* has become the *tester*. Invoked to decide the truth of a suspicion of transcendently high density in the "white dwarf" stars, it has decided that in the companion of Sirius matter is compressed to the almost incredible density of a ton to the cubic inch.

The other direction in which modern physical theory has broken away altogether from the ideas of the nineteenth century is in the quantum theory. Whilst there is nothing in the relativity theory too difficult to be mastered with sufficient effort, probably no one would claim that he really understands the quantum theory. For such illumination as we do possess we are in great measure indebted to Prof. Einstein. In 1905, almost at the same time as he published his first work on relativity, he put forward the famous law of the photo-electric effect, according to which the energy of a single quantum is employed in separating an electron from an atom and endowing it with kinetic energy. This was, perhaps, the first recognition that the development of the new quantum mechanics was not to be tied to classical mechanics by pictures of quasi-mechanical oscillators or other intermediate conceptions, but was to proceed independently on radically different principles. Noteworthy contributions followed, on the theory of ionization of material, and on the problem of the specific heats of solids. In 1917 Einstein reached another fundamental result—namely, the general equation connecting absorption and emission coefficients of all kinds. This gives deep insight into the origin of Planck's law of radiation, besides providing new formulæ with the widest practical applications.

If it is thought that Einstein's work of relativity deals with transcendental realms of thought with little bearing on the immediate needs of practical science, his work on the quantum theory has provided some of the most indispensable formulæ of daily application in the physical laboratory. But the truth is that both contribute to the development of physical science in its most practical mood; and both alike are distinguished by a penetrating insight into the origin and interconnection of the laws governing experimental phenomena.

A Royal Medal is awarded to Professor William Henry Perkin.

The science of organic chemistry owes a large debt to Prof. William Henry Perkin, as instance in recent years his monograph on cryptopine and protopine, a record of chemical research rarely equalled in experimental skill and precise reasoning. He has revealed the constitutions of the alkaloids harmine and harmaline ; he is nearing the solution of the structures of strychnine and brucine, two alkaloids which have hitherto resisted all attempts to determine their structural formulæ. His work on berberine has left few questions unanswered concerning the constitution of this important substance. Moreover, while developing new methods of attack on the chemistry of these natural products, he has faced many problems in structural organic chemistry, which, though aside from the main line of his work, he has with characteristic thoroughness solved by the aid of collaborators who have received their training under him.

He succeeded, during a period of twenty years at the University of Manchester, in building up there a school of chemical research which was a pattern to the country, and gave inspiration to many who were fortunate enough to study there under him. During the past twelve years, in the University of Oxford, he has again organized and developed a similar research school ; the records of the Dyson-Perrins Laboratory at Oxford, designed and equipped under his direction, bear witness to the extent and fruitfulness of the researches there carried out by him.

For his earlier work the Society, in 1906, awarded him the Davy Medal ; this Royal Medal is now awarded him in recognition of his more recent contributions to the science he has done so much to advance.

A Royal Medal is awarded to Professor Albert Charles Seward.

Professor Seward's work has been conspicuous on account of the way in which he has extended and reduced to order our knowledge of the palæobotany of Gondwanaland, especially in India, South and Central Africa, Antarctica and the Falkland Islands. The isolated descriptions of fragmentary fossils, which have accumulated in enormous quantities since McCoy, in Australia, and Feistmantel, in India, did their main descriptive work in the 'seventies, remained of local and limited stratigraphical value until further investigations showed that many fossil fragments previously described under separate generic names belonged to the same species. The important problem of correlating the widely separated Gondwana beds in India and on the three southern continents has been based largely on the plant remains, and has now attained a satisfactory stage on account of Professor Seward's work on material obtained from all the

areas concerned. The lower stages of the Gondwana system are characterised by evidences of a glacial climate ; and in order more completely to understand the conditions of life that existed, Professor Seward has visited Greenland and otherwise paid special attention to the effect of climate and light in explaining the rise and luxuriance of the Glossopteris flora in the Southern Hemisphere. In addition to its direct stratigraphical value to geologists, his work has added greatly to our knowledge of plant migration, and especially of the way in which the Glossopteris flora invaded the Northern Hemisphere, previously occupied by the groups familiar to us by our Coal Measure plants. He has thus utilised the principles and facts of one science to solve the problems of another.

The Davy Medal is awarded to Sir James Irvine.

The constitution of the simpler sugars (monosaccharoses) was based on a sure foundation by the classical researches of Emil Fischer. Taking up the investigation where Fischer had left it, Irvine was able, in the first instance in association with Purdie and later in conjunction with the many students who have received their training in research under him at the University of St. Andrews, to carry the enquiry into the more complex field of the disaccharoses, and by means of new processes, which he has been able to evolve and apply, to assign definite chemical structures to many of these most important natural products. Not content with this achievement, he has also studied the constitutions of the still more complex polysaccharoses, Starch and Inulin, and has been able to throw considerable light on the chemical structures of these substances, incidentally gaining an insight into the manner in which the plant forms and utilises these fundamental reserve materials.

The Sylvester Medal is awarded to Professor Alfred North Whitehead.

Whitehead's early work was strictly mathematical. He made important contributions to generalised algebra, in particular to the calculus of extension, to axiomatic geometry, to non-Euclidean geometry, to the theory of cardinals, and to the older forms of symbolic logic. Always primarily interested in the foundations of mathematics, it is in the logical analysis of these foundations that his main reputation has been won. The great work, *Principia Mathematica*, written in collaboration with Bertrand Russell, contains the most systematic and the most profound analysis to which the foundations of the subject have yet been submitted. In the three volumes of this work it is shown how all pure mathematics may be developed from a minimum of primitive ideas and fundamental propositions, of a purely logical kind, and a standard of accurate

reasoning is established, over the whole field of mathematical logic, comparable with that established by Weierstrass in the older mathematical analysis.

From pure mathematics both Whitehead and his collaborator have turned independently to physics. In his more recent books Whitehead has endeavoured to apply the spirit of *Principia Mathematica*, and in particular the principle which he calls "extensive abstraction," in the more complicated and more controversial field of physical existence. That a point, whether in the older physics or the modern physics of space-time, is a class, or a class of classes, of events, that an electron is a systematic correlation of the characters of all events throughout all nature, are doctrines at which the unsophisticated may be tempted to scoff. The tendency of modern scientific thought is to the conclusion that, if the world of physics is indeed ultimately capable of any rational interpretation, it must be interpreted in some such way. All those, whether mathematicians, philosophers, or physicists, who desire some orderly philosophy of physical nature, will recognise the very great importance of Whitehead's contribution to their common end.

The Hughes' Medal is awarded to Mr. Frank Edward Smith.

Mr. F. E. Smith has been awarded the Hughes' Medal in recognition of the value of his work towards realisation of the fundamental units of electrical measurement. His work on this subject began in 1902.

The results of these various investigations were published in a series of papers in the "Philosophical Transactions," and have remained as standard; such further experiments as have been made since have served only to confirm their accuracy. In words from a paper on the value of an ampere, published in 1912 by the Bureau of Standards of Washington, "The work marks a new epoch in the history of the absolute measurement of electrical quantities."

Other important investigations by Mr. Smith have dealt with the measurement of Terrestrial Magnetism. The recording magnetometers which he designed have proved of great value, while more recently he constructed, at the suggestion of Sir Arthur Schuster, a horizontal force magnetometer of extreme accuracy. During the war his services to the nation were of great importance, and since the Armistice, as Director of Research at the Admiralty, he has been responsible for a number of valuable investigations.

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*Studies in Catalytic Combustion.—Part II. The Union of Carbon Monoxide and Oxygen in Contact with Nickel, Copper and their Oxides.*

By WILLIAM A. BONE, D.Sc., F.R.S., and G. W. ANDREW, M.Sc.

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After investigating the action of gold in causing the union of carbon monoxide and oxygen at temperatures between  $275^{\circ}$  and  $325^{\circ}$  C., as already described in Part I of this series,\* we turned our attention to nickel, copper and their oxides, as examples of surfaces which certainly are not chemically indifferent to the reacting gases. For, as is well known, freshly reduced nickel forms a carbonyl with carbon monoxide at quite moderate temperatures ( $30^{\circ}$  to  $80^{\circ}$  C.), and copper (as we have found) is by no means indifferent to the gas at somewhat higher temperatures. Again, whilst copper very readily combines with oxygen at moderate temperatures, nickel is more resistant to oxidation, but, like iron, will burn if sufficiently heated in oxygen. Nickel, therefore, has a greater affinity for carbon monoxide, but a less affinity for oxygen, than has copper; also, their oxides are all readily reducible by carbon monoxide at moderate temperatures. Altogether, the properties of these two metals and their oxides are such as would seem to be highly conducive to "catalytic" activity towards mixtures of carbon monoxide and oxygen, if, in any circumstances, such activity is essentially chemical. Hence our choice of them for a detailed experimental study, the results of which are summarized in this paper.

The apparatus and experimental method employed were in all essential respects the same as those already detailed in Part I hereof, namely, the "circulation method" as introduced by Bone and Wheeler, with the inclusion of a suitable arrangement for continuously removing the reaction product ( $\text{CO}_2$ ) from the system by means of a solution of purified barium hydroxide. Also, the plan of recording the experiments in their chronological sequence will again be adopted, using the same symbols as before.

*A. Experiments with Nickel Gauze.*

The nickel was used in the form of a gauze of 10 strands per centimetre weighing about 100 grams, which in the Bone and Wheeler experiments had

\* 'Roy. Soc. Proc.,' A, vol. 109, pp. 459-476 (1925).

proved to be a most efficient catalyst for hydrogen-oxygen mixtures at temperatures even as low as  $220^{\circ}\text{C}.$ \* It was, however, found to be much less active towards CO-oxygen mixtures, a temperature about  $150^{\circ}$  higher being required before a conveniently measurable rate of combustion could be obtained.

Before commencing the experiments the gauze was reduced in hydrogen at dull red heat, in order to reduce any superficial film of oxide which might be present on its surface. It then assumed a bright metallic lustre, and on examination with a low-power lens it seemed to be quite smooth and free from pitting. In such condition it was introduced into the reaction tube of the "circulation apparatus" for the first experiment of the series at a temperature of  $365^{\circ}\text{C}.$  It soon reached a steady state of activity towards a "normal" mixture ( $2\text{CO} + \text{O}_2$ ) of the reacting gases, as shown in the following experiment (III). Also, as in all other cases hitherto examined by us, the rate of  $\text{CO}_2$ -formation proved to be proportional to the pressure of the dry "nitrogen-free" reacting mixture in the apparatus. No appreciable liberation of hydrogen occurred during the experiment, which circumstance, reinforced by other evidence obtained later, showed any  $\text{CO}_2$ -formation by direct interaction at the surface between carbon monoxide and steam to have been negligibly small.

Experiment III (9)† with mixture =  $2\text{CO} + \text{O}_2$  surface in normal state.

$$T = 365^{\circ}. \quad \theta = 21.9^{\circ}.$$

$t$	0	1	2	3	4	$8\frac{1}{2}$	Hours.
P	341	288	244	204	170	83	mm.
$k_1$	=	0.0734	0.0728	0.0744	0.0755	0.0720	

N.B.—About 15 per cent. of the original mixture had reacted during the first hour.

The apparatus was next thoroughly exhausted (with the gauze at  $365^{\circ}\text{C}.$ ) for 18 hours continuously, after which a mixture containing a large excess of carbon monoxide (original composition =  $4\text{CO} + \text{O}_2$  approx.) was introduced for Experiment IV (*vide infra*) which showed the  $\text{CO-Ni-O}_2$  system to be super-reactive, with the rate of  $\text{CO}_2$ -formation nearly proportional to the partial pressure of the CO throughout.

\* 'Phil. Trans.,' A, vol. 106, pp. 53-56 (1906).

† The Roman numeral denotes the actual sequence of each experiment, and the ordinary numeral in brackets the particular day in the series on which it was made.

## Experiment IV (13) with mixture containing a large Excess of Carbon Monoxide.

$$T = 368^{\circ}. \quad \theta = 20.2^{\circ} \text{ C.}$$

$t$ .	$P_{\text{CO}}$	$P_{\text{O}_2}$	$k_{\text{CO}}$	$k_{\text{O}_2}$
Hours.	mm.	mm.	—	—
0	331.0	82.3	—	—
1	261.5	47.6	0.1024	0.238
2	203.5	18.5	0.1056	0.323
3	174.5	4.0	0.0927	0.438
$x$	166.4	nil	—	—

The residual 166.4 mm. of carbon monoxide (*plus* 17.5 mm. water vapour) was afterwards continuously circulated over the heated gauze ( $T = 365$  to  $368^{\circ} \text{ C.}$ ) during the next three days, after which it was pumped out of the apparatus,\* and the reaction tube further exhausted for a few minutes. Another "normal" mixture  $2\text{CO} + \text{O}_2$  was thereupon introduced, and the following observations taken (Experiment V) which showed the CO-treated gauze to be at least two and a-half times as active as it had been in Experiment III.

Experiment V (16) with Mixture  $2\text{CO} + \text{O}_2$ . Surface super-active after prolonged CO-treatment.  $T = 370^{\circ}$ .  $\theta = 21.7^{\circ} \text{ C.}$ 

$t$ .....	0	1	2	3	Hours.
$P$ .....	428	255	143	74	mm.
$k_1$ .....	—	0.225	0.238	0.254	

N.B.—About 40 per cent. of the original mixture had reacted during the first hour (*c.f.* Experiment III).

Another noteworthy circumstance was that the "super-normal" activity thus acquired by the metal hardly diminished after a five days' subsequent continuous exhaustion of the apparatus; for at the end of it  $k_1$  for a  $2\text{CO} + \text{O}_2$  mixture remained as high as from 0.18 to 0.22 (Experiment VI,  $T = 370^{\circ}$  on 21st day), and was not altered (Experiment VII,  $T = 375^{\circ}$  on 23rd day) by a further two days' continuous exhaustion at the experimental temperature. This should be contrasted with the behaviour of gold in like circumstances (*vide* Part I *loc. cit.*, pp. 469 and 471), where a similarly imparted CO-stimulus

\* It should be noted that at the end of this three days' "circulation" the residual gas (which originally and at the conclusion of Experiment II was hydrogen-free) was found to contain about 5.7 per cent. of hydrogen, pointing to some slight occurrence of the  $\text{CO} + \text{OH}_2 \rightleftharpoons \text{CO}_2 + \text{H}_2$  interaction during the prolonged CO after-treatment.

was greatly diminished, though not entirely removed, by subsequent prolonged exhaustion.

The "super-normal" activity of the surface, and the proportionality of the rate of  $\text{CO}_2$ -formation to the partial pressure of the CO, when excess of the last-named is present, were confirmed by the following further experiment.

Experiment VIII (24) with Mixture containing a large Excess of Carbon Monoxide.  $T = 375^\circ$ .  $\theta = 20.7^\circ$ .

$t$	$P_{\text{CO}}$	$P_{\text{O}_2}$	$k_{\text{CO}}$	$k_{\text{O}_2}$
Hours.	mm.	mm.		
0	323	81.6	—	—
1	231	35.8	0.145	0.358
2	177	8.4	0.130	0.544
$x$	161.5	nil	—	—

The residual 161.5 mm. of CO having been subsequently circulated over the surface at  $375^\circ \text{C}$ . for four days, and then pumped out of the apparatus as rapidly as possible, the value of  $k_1$  for a mixture  $2\text{CO} + \text{O}_2$  was found (Experiment IX,  $T = 375^\circ$  on 28th day) still to be 0.21, or practically the same as it was after Experiment V.

The explanation of the foregoing facts became evident as soon as the gauze was examined at the conclusion of Experiment IX. For it was found to have completely changed in appearance, its former metallic lustre having given place to a uniform dull brownish colour in the middle, gradually shading off to bright blue at either end, without, however, any patchy area being noticeable. On being subsequently heated in a vacuum tube to dull redness, the original metallic lustre of the surface was completely restored, about 1.7 c.c. of carbon dioxide (not the monoxide) being collected during the operation. Such circumstances pointed to the formation of a highly reactive surface film of nickel-carbonyl, or possibly oxy-carbonyl, during the fourth and subsequent experiments, which accounted for the enhanced catalytic activity of the surface.

On afterwards circulating a mixture  $2\text{CO} + \text{O}_2$  over the thus "re-conditioned" gauze (Experiment X,  $T = 375^\circ$ ) the metal was still found to be in a super-normally active condition.

Experiment X (38) with Mixture  $2\text{CO} + \text{O}_2$  over "Reconditioned" Gauze.

$$T = 375^\circ \text{C.} \quad \theta = 19.0^\circ.$$

$t$ .....	0	$\frac{1}{2}$	$1\frac{1}{4}$	$2\frac{1}{4}$	Hours.
P .....	373	266	161	76	mm.
$k_1$ .....	—	0.293	0.292	0.307	

That no appreciable amount of hydrogen is liberated during the catalytic combustion at this temperature was confirmed by an explosion analysis of the residual gas at the conclusion of this experiment, which gave a C/A ratio = 0.501, pure carbon monoxide requiring 0.500.

On re-examining the gauze at the conclusion of Experiment X, it was again seen to be uniformly and completely covered with a brownish surface film; but its original lustre was again entirely restored, with the evolution of carbon dioxide, when the metal was subsequently heated to dull redness. The following three experiments (XI to XIII) concluded the series, from which it will be seen (1) that in Experiment XI, where a normal  $2\text{CO} + \text{O}_2$  mixture was circulated over the newly "reconditioned" gauze, the velocity constant indicated a state of activity about midway between those exhibited in Experiments III and V respectively; (2) that in Experiment XII, where a mixture containing excess of CO was employed, the catalytic activity (as indicated by the  $k_{\text{O}_2}$  values) progressively increased, the rate of  $\text{CO}_2$ -formation being again proportional to the partial pressure of the carbon monoxide, and (3) that in Experiment XIII, where the normal mixture  $2\text{CO} + \text{O}_2$  was circulated over the gauze immediately after it had been subjected to a CO treatment for four days at the experimental temperature, the catalytic activity was practically the same as in Experiment V, indicating that in all probability the actual surface area exposed to the gases had not materially altered during the series.

	Mixture employed.	Gauze.	T.	$\theta$ .	Results.
Experiment XI (44)...	$2\text{CO} + \text{O}_2$ .....	Re-conditioned	$376^\circ$	$22.5^\circ$	$k_1 = 0.150$ constant.
Experiment XII (49)	Excess CO in Mixture (initially $4\text{CO} + \text{O}_2$ )	—	$376^\circ$	$22.0^\circ$	$k_{\text{CO}} = 0.097$ to $0.107$ $k_{\text{O}_2} = 0.227$ to $0.430$
Experiment XIII (54)	$2\text{CO} + \text{O}_2$ .....	After CO-treat- ment, 4 days	$373^\circ$	$20.2^\circ$	$k_1 = 0.20$ , rising to $0.25$ .

The evidence of these experiments, taken as a whole, certainly shows that the formation of a reactive Ni-CO, or possibly O-Ni-CO, complex in the surface layer is, or in definable circumstances may become, a prime factor in the catalytic combustion, which in such circumstances may be visualised as involving interactions in either a CO-Ni-O system, or, alternatively, between a Ni-carbonyl complex, primarily formed in the surface layer, and adsorbed or atomised oxygen. There was unquestionable proof of the formation of such complexes in the surface layer, which justifies the view that the catalytic action of nickel is, or may be, of a more chemical type than is the case with gold. But whilst this is admittedly so, there were other features of the experiments which suggested that the catalytic actions of nickel may really be of a dual character, involving on the one hand (a) the "activation" by the metal of the two gases marked by a comparatively low rate of CO<sub>2</sub>-formation, as in Experiment III, and, on the other hand, (b) the intermediate formation of still more reactive CO-Ni-O complexes, as in Experiment V. But whether or no (a) really occurs independently of (b) was perhaps not conclusively demonstrated, and further investigation of the matter is in progress. At all events, the conclusion which Langmuir drew from his experiments with platinum, namely, that CO<sub>2</sub>-formation takes place only when unadsorbed CO molecules from the surrounding atmosphere strike atomised O condensed on the surface, manifestly cannot be extended to the case of a nickel surface under the conditions of our experiments.

#### B. Experiments with Copper Gauze.

The case of copper proved to be particularly interesting, inasmuch as, in a freshly-reduced condition, it was a more active catalyst than nickel. On the other hand, after treatment with CO at a comparatively low temperature it became covered with a film composed of a fairly stable Cu<sub>2</sub>CO complex, in which condition, however, it was (unlike nickel) very unreactive.

*1st Series.* T = 135° C.—Before commencing this series, the copper gauze employed had undergone a preliminary treatment during which it was first of all superficially oxidised *in situ* at a moderate temperature in a current of air, and afterwards thoroughly reduced in hydrogen at 370° C. In such a freshly-reduced condition, it was fairly reactive at 135° C. towards "normal" mixtures of carbon monoxide and oxygen (2CO + O<sub>2</sub>). In each case the rate of combination, though nearly proportional to the partial pressure of the dry "nitrogen-free" gases, tended to diminish with time, as the

following two experiments, made in the first and fourth days of the series, indicate :—

Experiments I and II (1) and (4) with Mixture  $2\text{CO} + \text{O}_2$ .

$T = 135^\circ$ ,  $\theta = 13.2^\circ$ .

I.			II.		
<i>t.</i>	<i>p.</i>	<i>k<sub>1</sub></i>	<i>t.</i>	<i>p.</i>	<i>k<sub>1</sub></i>
Hours.	mm.		Hours.	mm.	
0	399	—	0	406	—
1	298	0.1268	1	326	0.0953
2	241	0.1095	2	276	0.0838
3	200.5	0.0997	3	232	0.0808
4	161.5	0.0982	4	195	0.0796
5	125.0	0.1020	8	102	0.075

No hydrogen could be detected in the residual gases removed from the apparatus at the end of each experiment, and no more oxygen disappeared than was required to combine with the CO burnt in either case. Therefore, it may be concluded that no appreciable permanent oxidation of the surface took place with such "normal" mixtures at this temperature.

After a mixture originally containing a large excess of carbon monoxide ( $4\text{CO} + \text{O}_2$ ) had been circulated over the gauze (Experiment III on 11th day), and the 162 mm. residual CO (after all the oxygen had disappeared) had been kept circulating over it for six days longer, the surface had become completely coated with a film, brownish for the most part, but steel-blue in places, which on subsequent examination proved to be a  $\text{Cu} \cdot \text{CO}$  (or  $\text{O} \cdot \text{Cu} \cdot \text{CO}$ ) complex entirely decomposable when heated *in vacuo* to between  $400^\circ \text{C}$ . and  $500^\circ \text{C}$ ., with evolution of carbon dioxide and complete restoration of the characteristic metallic appearance of copper. A final Experiment IV (on 17th day), in which a normal mixture ( $2\text{CO} + \text{O}_2$ ) was circulated at  $135^\circ$  over the gauze coated with the said complex, showed the surface to be only about one-fifth as reactive as it had been originally when freshly reduced in hydrogen at the outset of the series, the value of  $k_1$  being now only 0.023 as compared with 0.126 then.

*Second Series.*  $T = 250^\circ \text{C}$ .—Immediately before this series, the gauze had been heated to  $500^\circ \text{C}$ . in a current of carbon monoxide, during which it had become coated once more with the brownish film already referred to, and afterwards *in vacuo* at the same temperature in order to decompose the

Cu . CO (or possibly O . Cu . CO) complex. During this operation evidence was forthcoming of the volatility of said complex, for a film of copper was found on the walls of the tube in the vicinity of the gauze, and some minute brownish oily drops condensed in the cooler parts. On being heated *in vacuo*, these drops decomposed depositing a gold-coloured film on the glass. The bright copper-appearance of the gauze having been thus completely restored, it was quickly transferred to the circulation apparatus, for the following experiments :

Experiment I (1), with "Normal" Mixture  $2\text{CO} + \text{O}_2$  over Fresh Cu-surface.

$$T = 250^\circ. \quad \theta = 15.1^\circ.$$

$t$ .....	0	$\frac{1}{2}$	1	$1\frac{1}{2}$	Hours
P .....	289.0	198.0	139.0	96.0	mm.
$k_1$ .....	—	0.328	0.317	0.319	

On examining the gauze at the end of this experiment, no sign of any surface oxidation or carbonyl formation could be detected, although a mirror of copper (very slightly oxidised) was noticed on the walls of the reaction tube adjacent to the gauze.

Experiment II (5), with a Mixture containing Large Excess of Carbon Monoxide.  $T = 250^\circ. \quad \theta = 17.0^\circ.$

$t$ .	$p_{\text{CO}}$	$p_{\text{O}_2}$	$k_{\text{CO}}$	$k_{\text{O}_2}$
Hours.	mm.	mm.		
0	355	85	—	—
1	336	75	0.0239	0.0548
2	310	62	0.0284	0.0685
3	284	50	0.0323	0.0768
4	262	39	0.0330	0.0846
8	208	12	0.0290	0.1064
$x$	185	nil	—	—

It should be observed (i) that whilst the rate of combination was much more proportional to  $p_{\text{CO}}$  than to  $p_{\text{O}_2}$ , (ii) the gauze was much less reactive than in the previous experiment with the normal mixture  $2\text{CO} + \text{O}_2$ , although (iii) the values  $k_{\text{O}_2}$  shows that its catalysing power was progressively increasing during the whole experiment.

After the residual CO from Experiment II had been kept circulating over the gauze at  $250^\circ$  for three days, in order to cover the surface with the Cu . CO complex, it was withdrawn as quickly as possible, and a fresh "normal" mixture



2CO + O<sub>2</sub> introduced into the apparatus, with the following most significant results :—

Experiment III (8) with Mixture 2CO + O<sub>2</sub> over Surface after prolonged CO-treatment. T = 250°.  $\theta = 15.3^\circ$  to  $16.2^\circ$ .

<i>t</i>	0	1	2	3	4	5	Hours.
P	445	428	345	261	176	121	mm.
<i>k</i> <sub>1</sub>	—	0.017	0.056	0.077	0.100	0.113	

Experiment IV (9), with Mixture 2CO + O<sub>2</sub>. T = 250°.  $\theta = 15.7^\circ$ .  
Surface in same condition as at end of III.

<i>t</i>	0	1	2	3	4	Hours.
P	423	330	232	164	116	mm.
<i>k</i> <sub>1</sub>	—	0.108	0.130	0.137	0.140	

At the conclusion of IV, the gauze was taken out of the reaction tube and thoroughly oxidised by heating it for some hours in a separate apparatus to redness in a current of oxygen, after which it was replaced in the circulation apparatus where the catalysing power of the now oxidised surface towards a mixture of 2CO + O<sub>2</sub> at from 255 to 265° C. was determined as follows :—

Experiment V (20), with Mixture 2CO + O<sub>2</sub> over the Oxidised Gauze.  
T = 255° to 265°.  $\theta = 16.25^\circ$ .

<i>t</i>	0	1	2	3	4	Hours.
P	379	266	196	144	103	mm.
<i>k</i> <sub>1</sub>	—	0.154	0.143	0.140	0.141	

The significance of the foregoing experiments lies in the outstanding fact that, whereas in I to IV the oxygen in the reacting gaseous mixtures apparently did not chemically combine with the copper at the surface, the latter became coated with a film of volatile Cu.CO complex, to the detriment of its catalysing power, which was at its maximum when free from such film. Moreover, the "oxidised" surface in V was much less active than was the freshly-reduced surface in I, though much more so than was the "carbonyled" surface in III. And the conclusions which seem naturally to follow are :—(1) That the most vigorous oxidation of the carbon monoxide took place when it was "activated" merely by "occlusion" in the metal (i.e., before it assumed a Cu-carbonyl form), in which condition it readily combined with similarly

"occluded" and "activated" oxygen, and (2) that, for the real "catalytic" reaction, apparently no prior formation of either copper oxide or any  $\text{Cu} \cdot \text{CO}$  complex was required, but only the "occlusion" of the respective gases.

*C. Experiments with the Oxides of Nickel and Copper.*

In investigating the actions of the oxides of nickel and copper, we have kept in view the important question whether they depend upon oxygen chemically combined (as oxide) with the metal, or merely upon an adsorbed "activated" film of it. And in this connection it may be recalled that, from their experiments upon the catalytic actions of these oxides towards hydrogen-oxygen mixtures, Bone and Wheeler concluded (*loc. cit.*, pp. 59 to 67) that they depend upon the condensation of a film of "active" oxygen upon the surface, which, in the case of copper oxide, actually prevents the hydrogen from reducing the oxide. Therefore it seemed important to ascertain by direct experiment whether or no the same view would hold good also in the case of  $\text{CO}$ -oxygen mixtures in contact with such oxides.

We therefore set out first of all to discover *whether or no there is any range of temperature within which either or each of the two oxides in question will respectively act as an efficient catalyser towards a normal  $2\text{CO} + \text{O}_2$  mixture without itself undergoing any permanent change (i.e., either reduction or peroxidation).* And, after a series of careful trials, it was found that at  $150^\circ \text{C}$ . in the case of nickel oxide, and at  $170^\circ \text{C}$ . in the case of copper oxide, this important condition was fulfilled. These temperatures were, therefore, respectively selected as being conducive to the investigation of the true catalytic process in each case. And we will now proceed to summarise our experimental results.

(i) *With Granular Nickel Oxide at  $150^\circ \text{C}$ .—*The oxide was employed in the form of grey porous granules containing 99 per cent. of  $\text{NiO}$ , which previously had been heated at  $560^\circ \text{C}$ . in a current of oxygen so as to ensure the surface being in a properly oxidised state. Thus prepared, it was packed into the reaction tube of the circulation apparatus, where its temperature was maintained at between  $147$  and  $150^\circ \text{C}$ . day and night throughout the following series of experiments.

Throughout each of these experiments (*vide infra*) not only was the rate of  $\text{CO}_2$ -formation remarkably constant, and proportional to the pressure of the reacting mixture, but also analysis of the residual gaseous mixture at the end of the experiment showed that the process *had been unattended by any appreciable reduction of the  $\text{NiO}$  at the surface*, because no more of the  $\text{CO}$  had disappeared than actually sufficed to combine with the  $\text{O}_2$  used up.

Experiments I and II (1 and 2) with Mixture  $2\text{CO} + \text{O}_2$ . $T = 148^\circ$ .  $\theta = 22^\circ \text{C}$ .

I (1).			II (2).		
$t$ Hours.	P mm.	$k_1$	$t$ Hours.	P mm.	$k_1$
0	421	—	0	425	—
1	304	0.141	$\frac{1}{2}$	360	0.144
$1\frac{1}{2}$	257	0.143	1	304	0.145
3	155	0.145	$1\frac{1}{2}$	254	0.149
4	107	0.149			

Immediately on the conclusion of II, another experiment (III) was started in which a mixture containing a large excess of oxygen (originally  $\text{CO} + \text{O}_2$ ) was employed. The resulting rate of  $\text{CO}_2$ -formation (*vide infra*) showed the surface to be super-normally active; and although it was not throughout proportional to the partial pressure of either of the two reacting gases, the catalysing power of the surface was progressively stimulated by the increasing excess of oxygen as the experiment proceeded.

## Experiment III (2) with Mixture containing Excess Oxygen.

 $T = 148^\circ$ .  $\theta = 23.4^\circ$ .

$t$	$p_{\text{CO}}$	$p_{\text{O}_2}$	$k_{\text{CO}}$	$k_{\text{O}_2}$
Hours.	mm.	mm.		
0	231	218	—	—
1	149	177	0.190	0.0905
2	89	147	0.207	0.0916
3	44	125	0.240	0.0805
$4\frac{1}{2}$	11	108	0.294	0.0678
$x$	nil	103.5	—	—

The residual oxygen (103.5 mm.) was then kept circulating continuously over the surface at  $147^\circ$  for a further period of 40 hours, after which it was rapidly pumped out of the apparatus, and another charge of the "normal"  $2\text{CO} + \text{O}_2$  mixture re-introduced (Experiment IV) (4). The surface was now found to be, if anything, rather more than normally active ( $k_1 = 0.147$  rising to 0.182).

A repetition of Experiments III and IV gave similar results; for when in Experiment V (5) a mixture initially containing  $\text{CO} + \text{O}_2$  was again admitted to the apparatus ( $T = 150^\circ$ ,  $\theta = 34^\circ \text{C.}$ ),  $k_{\text{CO}}$  at the outset was equal to 0.174, afterwards rising to 0.241, whilst  $k_{\text{O}_2}$  at the outset was equal to 0.076, afterwards falling to 0.061 in 4 hours. Finally, after the residual oxygen had been circulated over the surface at  $150^\circ$  for a period of 60 hours, and then rapidly pumped out, the  $k_1$  value for a mixture  $2\text{CO} + \text{O}_2$  at  $150^\circ \text{C.}$  (Experiment VI) was found to be 0.155 (*vide infra*), showing the surface to be only slightly more than normally active after the long  $\text{O}_2$ -treatment.

Experiment VI (8) with Mixture  $2\text{CO} + \text{O}_2$  after  $\text{O}_2$ -treatment.

$T = 148^\circ$ .  $\theta = 26.3^\circ$ .

$t$	0	1	2	3	4	Hours.
P	493	344	242	173	119	mm.
$k_1$	—	0.156	0.153	0.151	0.154	

Having thus proved that at  $150^\circ \text{C.}$  a fairly rapid catalytic  $\text{CO}_2$ -formation occurred without any appreciable reduction of the  $\text{NiO}$ , it now remained to ascertain the rate of reduction of the  $\text{NiO}$  by  $\text{CO}$  at the same temperature in absence of free oxygen. For this purpose nothing more was needed than to circulate a mixture of  $2\text{CO} + \text{N}_2$  over the surface at  $150^\circ$ , and to compare the rate of  $\text{CO}_2$  formation in such circumstances with that already ascertained in the case of the  $2\text{CO} + \text{O}_2$  mixture (*cf.* Experiments I, II and IV) at the same temperature. Accordingly, the following experiment (VII) was made:—

Experiment VII (13), showing Rate of Reduction of the Surface by  $2\text{CO} + \text{N}_2$

Mixture.  $T = 150^\circ$ .  $\theta = 25^\circ$ .

$t$	0	1	2	8	21	Hours.
P	470	461	454	453	446	mm.

*i.e.*, Total  $\text{CO}_2$  formation in 21 hours = 24 mm., as compared with 100 mm. in 1 hour for the  $2\text{CO} + \text{O}_2$  mixture in VI.

The rate of reduction of the nickel oxide by carbon monoxide under the experimental conditions having thus been proved to be negligibly small (only 24 mm. of  $\text{CO}_2$  were formed in 21 hours), sufficient oxygen was now added to the residual gas from VII to bring its composition up to  $2\text{CO} + \text{N}_2 + \text{O}_2$  approximately, the temperature of the surface being kept at  $150^\circ \text{C.}$  The

*immediate effect of such addition of oxygen (Experiment VIII (13)) was a great acceleration in the rate of CO<sub>2</sub> formation, as the following observations show:—*

Experiment VIII (13) with Mixture originally = 2CO + N<sub>2</sub> + O<sub>2</sub>.

T = 148°. θ = 25.7°.

<i>t</i>	0	1	2	3½ Hours.
P	192	134	96	67 mm.
<i>p</i> (2CO + O <sub>2</sub> )	137	79	41	12 mm.
<i>k</i> (2CO + O <sub>2</sub> )	—	0.239	0.262	0.302

We regard the foregoing results, which are in entire agreement with those obtained by Bone and Wheeler (*loc. cit.*) when investigating catalytic actions of a similar nickel-oxide surface towards hydrogen-oxygen mixtures, as being incompatible with the idea that the catalytic process involves a rapidly alternating series of oxidations and reductions of the surface. On the contrary, they strongly support the view that it involves the formation of a film of "active" oxygen at the surface as the effective oxidising agent. It was, indeed, such an "activated-oxygen" film, and not the NiO itself, which chiefly burnt the carbon monoxide in our experiments. This activated O-film seemed to be almost instantaneously formed at the surface, but not necessarily all over it. For doubtless CO molecules were also attracted to the surface, but, being relatively unreactive towards the NiO, would probably remain there for some time unoxidised, thus hindering, to some extent, the free access of fresh O<sub>2</sub> molecules to the surface, and therefore their "activation." Hence, with a mixture 2CO + O<sub>2</sub> a steady state of surface reactivity was usually quickly reached and easily maintained (*vide* Experiments I, II and VI); but, in cases where the ratio O<sub>2</sub> : CO in the outer atmosphere progressively increased during an experiment (*vide* III and V), proportionately more O<sub>2</sub> and less CO molecules would hit the surface in a given time, so that an increasingly larger portion of its area would become coated with the "activated O film," with consequent enhancement of the catalysing power of the surface (*vide* the progressively increasing *k*<sub>CO</sub> values in Experiments III and V).

(ii) *With Granular Copper Oxide at 165° to 175° C.*—The reaction tube of the apparatus was packed with the same granular copper oxide as used by Bone and Wheeler in their hydrogen-oxygen experiments (*loc. cit.*, p. 66), it having just previously been heated to dull redness in a current of oxygen to ensure its surface being well oxidised. On circulating a charge of a mixture 2CO + O<sub>2</sub> over the surface (T = 166.8° C.) immediately after the aforesaid

oxygen treatment (Experiment I), it was found to be rather supernormally active ( $k = 0.18$ ). Thinking that this might possibly be due to the surface having been somewhat "super-saturated" by an "activated O film" during the preliminary  $O_2$  treatment, it was kept well exhausted at  $165^\circ C.$  for two days in order to minimise any such possible effect. On again admitting a charge of  $2CO + O_2$  mixture into the apparatus (Experiment II), a perfectly regular series of  $k_1$  values was obtained, the surface by that time having settled down to a "normal" condition, and the rate of combination being strictly proportional to the pressure of the reacting gaseous mixture, as follows:—

Experiment II (4) with Mixture =  $2CO + O_2$ .  $T = 166^\circ$  to  $168^\circ$ .  $\theta = 12.0^\circ$ .

$t$	0	1	2	3	4	5 Hours.
P	415	311	227	168	121	90 mm.
$k_1$	—	0.125	0.131	0.131	0.134	0.133

N.B.—Approximately 25 per cent. of the CO disappeared during the first hour.

Incidentally, it was also proved (1) that the ratio  $CO : O_2$  remained constant at 2:1 throughout such an experiment, implying that the surface itself was neither oxidised nor reduced during the catalytic combination of the gases and (2) that no hydrogen was liberated as the result of any  $CO + OH_2 \rightleftharpoons CO_2 + H_2$  interaction.

In the next experiment (III), a mixture containing excess of oxygen was admitted to the apparatus, with the following results, which showed the rate of combination to be quite normal, and very nearly proportional to the partial pressure of the carbon monoxide throughout.

Experiment III (6), Mixture originally =  $CO + O_2$ .  $T = 165^\circ$ .  $\theta = 14.5^\circ$ .

$t$	$p_{CO}$	$p_{O_2}$	$k_{CO}$	$k_{O_2}$
Hours.	mm.	mm.		
0	197	220	—	—
1	152	197	0.113	0.0442
2	114	180	0.119	0.0455
4½	54	148	0.125	0.0396
6½	31	137	0.129	0.0340
7½	23	133	0.128	0.0307
$x$	nil	121.5	—	—

The results of this experiment having been confirmed by those of a precisely similar one (V), we next proceeded in two following experiments (VI and VII)

to compare the effects upon the catalysing power of the surface by first of all circulating oxygen over it at  $165^{\circ}$  for a period of from 30 to 40 hours, and then exhausting it at such temperature (a) in the one case for 10 minutes only, and (b) in the other continuously for four days, before subsequently testing its activity towards a  $2\text{CO} + \text{O}_2$  mixture. In this way it was hoped to demonstrate the influence of any "activated-O-film" which might be operative in the catalytic process; and the results of the two experiments (*vide infra*) fully realised this expectation, the surface being initially about twice as active in VI as it was in VII, thus:—

Comparison of Catalysing Powers of the CuO-Surface towards  $2\text{CO} + \text{O}_2$  at  $165^{\circ}$  after prolonged exposure to  $\text{O}_2$  followed by subsequent Exhaustion at such Temperature for—

(a) 10 Minutes.			(b) 4 Days.		
Expt. VI (16), $T = 167^{\circ}$ .			Expt. VII (21), $T = 165^{\circ}$ .		
<i>t.</i>	P.	$k_1$ .	<i>t.</i>	P.	$k_1$ .
Hours.	mm.		Hours.	mm.	
0	388	—	0	404	—
$1\frac{1}{2}$	204	0.186	$1\frac{1}{2}$	317	0.084
$2\frac{1}{2}$	137	0.180	2	268	0.089
$6\frac{1}{2}$	46	0.150	3	215	0.091
			5	109	0.114

It was thus demonstrated that the catalysing power of the oxygen-treated surface was considerably reduced by subsequent prolonged exhaustion. And, inasmuch as such exhaustion presumably could not have affected the oxide itself, but only such adherent "activated-oxygen" film as the previous oxygen-treatment had occasioned, the natural conclusion is that, as in the case of the nickel oxide surface, such an O-film, and not the CuO, was really the effective oxidising agent when the normal  $2\text{CO} + \text{O}_2$  mixture was subsequently circulated over the surface.

Two days after Experiment VII, we determined the rate of reduction of the CuO at  $165^{\circ}$  by circulating over the surface a mixture approximately  $2\text{CO} + \text{N}_2$ ; this was found to be so fast, in comparison with the rate of  $\text{CO}_2$ -formation with the  $2\text{CO} + \text{O}_2$  mixture in any of the previous experiments

of the series, that it was now necessary to read the manometer every few minutes, as follows :—

Experiment VIII (23), showing Rate of Reduction of Surface by Mixture  
 $2\text{CO} + \text{N}_2$ .  $T = 162$  to  $165^\circ$ .  $\theta = 17.2^\circ$

Time.	P.	$P_{\text{CO}}$ .	$k_{\text{CO}}$ .
Minutes.	mm.	mm.	—
0	375.8	224	
1	364.8	215	1.068
5	349.8	200	0.590
10	335.8	186	0.498
20	313.8	164	0.406
30	293.8	144	0.383
60	248.3	98.5	0.357
120	191.8	42.0	0.363
150	178.3	28.5	0.358
$\infty$	149.8	nil	—

N.B.—Approximately 56 per cent. of the CO disappeared in the first hour.

It may here be recalled that the great disparity thus brought about between the rates of  $\text{CO}_2$ -formation when each of the two mixtures  $2\text{CO} + \text{O}_2$  and  $2\text{CO} + \text{N}_2$ , respectively, were circulated over the surface at  $165^\circ$  (compare Experiments I and VIII) is closely paralleled by the corresponding observations of Bone and Wheeler (*loc. cit.*, p. 61) upon the rates of  $\text{H}_2\text{O}$ -formation when mixtures  $2\text{H}_2 + \text{O}_2$  and  $2\text{H}_2 + \text{N}_2$ , respectively, were circulated over the same CuO surface at  $200^\circ$ . For they found that, whereas about 50 per cent. of the original hydrogen disappeared in the first hour with the mixture  $2\text{H}_2 + \text{N}_2$ , only 9.7 per cent. was burnt in the same time when the mixture  $2\text{H}_2 + \text{O}_2$  was used, there being no reduction at all of the CuO in the latter case. We thus conclude, as they did, that the real catalytic combination of combustible gas and oxygen over a CuO surface would appear not only to involve the condensation of a film of "active" oxygen at the surface, but that this film actually protects the catalysing surface from the attacks of the combustible gas which would otherwise energetically reduce it.

The foregoing conclusion was confirmed by an interesting series of observations made at a later date by one of us (W.A.B.) in conjunction with Dr. Harold Hartley, in the course of an investigation upon the influence of water vapour during the catalytic combination of carbonic oxide and oxygen over a similar granular copper oxide surface at a temperature of  $200^\circ$ . And, with his concurrence, we will now briefly indicate their purport.



It was found that not only oxygen but also nitrogen will condense and form a protective film on a copper oxide surface at such temperatures as we have used; but whereas such a nitrogen film, being inert towards the combustible gas, merely "blankets," and so puts out of action for the time being, any part of the surface upon which it is condensed, such an oxygen film, being "active" towards the combustible gas, becomes a prime factor in the catalytic combustion. And in conformity with this view of the matter, it was shown experimentally that the apparent catalysing power of a CuO surface towards a normal  $2\text{CO} + \text{O}_2$  mixture at  $210^\circ$  may be varied considerably merely by previously exposing it for a few hours to (a) air, or (b) oxygen, at moderate temperatures, or (c) by thoroughly exhausting it beforehand. Thus in a series of successive experiments, all similarly carried out, except for the stated variations in the "preliminary treatment" of the surface, the following significant results were obtained:—

Preliminary Treatment of Surface.	$k_1$ for $2\text{CO} + \text{O}_2$ Mixture in 1st hour.
(1) Exposure to air at $210^\circ$ for 16 hours.....	0.006
(2) Exposure to oxygen at $450^\circ$ for three hours ..	0.020
(3) Exhaustion for 21 hours following air-treatment at $210^\circ$ .....	0.0116

$\left. \begin{array}{l} T = 210^\circ \text{ C.} \\ \theta = 17^\circ \text{ C.} \end{array} \right\}$

It was thus established that what may be termed an "air-normalised" copper oxide surface has apparently a lower catalysing power than one which has been "oxygen-normalised," a circumstance which we think may be attributed to the "air-normalised" surface being partly blanketed by an inert condensed nitrogen film, so that it is only partly covered with the active O-film whereas an "oxygen-normalised" surface is wholly so covered. Moreover, prolonged evacuation of an "air-normalised" surface invariably increased its catalysing power, usually, however, to a point below that of a freshly "oxygen-normalised" surface.

Many other experiments also showed (1) that the rate of reduction, as measured by  $\text{CO}_2$ -formation over an "air-normalised" copper oxide surface, by a  $2\text{CO} + \text{N}_2$  mixture at  $200^\circ$ , and (2) the initial rate of re-oxidation of such a surface, after it has been thoroughly so reduced, are both of them many times greater than the rate of combination of a  $2\text{CO} + \text{O}_2$  mixture over the same CuO surface at the same temperature. Thus it was found that:—

Rate of	When circulated at 210° over	Initial Value of $k_1$
(1) $\text{CO}_2$ - formation from $2\text{CO} + \text{O}_2$	(a) the "air-normalised" CuO surface.....	0.0076
	(b) the " $\text{O}_2$ -normalised" CuO surface.....	0.0215
	(c) the "well exhausted" CuO surface.....	0.0116
(2) $\text{CO}_2$ - formation from $2\text{CO} + \text{N}_2$	the "air-normalised" CuO surface .....	0.7 to 0.8
(3) $\text{O}_2$ -disappearance from oxygen.	the freshly reduced CuO sur- face .....	0.24

It seems to us that these results can only mean that the active O-film is of more than monomolecular thickness, and we visualise the matter as follows. When a mixture of carbon monoxide and oxygen is circulated over a surface composed of the oxide of nickel or copper under conditions like those of our experiments, an activated O-film probably of more than monomolecular dimensions is formed at the surface. This film not only oxidises the carbon monoxide, but also effectively prevents the latter from penetrating to the underlying oxide surface and reducing it. Previous prolonged exposure of the surface to oxygen at the experimental temperature probably increases the thickness of the active O-film, and consequently also the catalysing power of the surface. On the other hand, a prolonged exhaustion of the surface at the same temperature with a pump of the type employed by us would probably diminish the thickness of the film and thus reduce the catalysing power of the surface; but the adherence of the film to the surface is apparently so strong that it would require a longer and more effective evacuation of the surface than we were able to make in our experiments entirely to remove it. This is probably why a well evacuated copper oxide surface burns the carbon monoxide of a  $2\text{CO} + \text{O}_2$  mixture very much more slowly than it does that of a  $2\text{CO} + \text{N}_2$  mixture at the same temperature.

Taken as a whole, the various experiments described in this paper constitute, in our opinion, a strong body of evidence supporting the supposition that the real catalytic combination of carbon monoxide and oxygen over the surfaces in question is a process different from, and independent of, either the oxidation of a primarily formed "carbonyl" film or the reduction of a metallic

oxide; although in certain circumstances, one or other of the last-named processes may occur simultaneously with it.

We conclude that, certainly in the case of copper and probably also in the case of nickel, the real catalytic combination does not necessarily involve any intermediate "oxide" or "carbonyl" formation, but only the "occlusion" of the respective gases. And in the cases of their oxides, we regard the evidence, whilst conclusive against the theory that the catalysing process consists of rapidly alternating reductions and re-oxidations of the surface, as confirming the idea that it involves the formation of an active O-film at the surface.

In conclusion, we desire to acknowledge our indebtedness to the Government Grant Committee of the Society for grants out of which part of the expenses of the investigation have been defrayed.

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### *The Crystalline Structure of Chrysoberyl.*

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1. Chrysoberyl,  $\text{BeAl}_2\text{O}_4$ , is analogous in chemical composition to spinel,  $\text{MgAl}_2\text{O}_4$ , and the other members of the spinel group, but it bears no resemblance to them in its crystalline form. The spinels are cubic, and have a very simple structure, which has been analysed by S. Nishikawa\* and W. H. Bragg.† The same type of structure has been discovered in other compounds.‡ Chrysoberyl belongs to the orthorhombic holohedral class, the axial ratios being  $a:b:c = 0.4707:1:0.5823$ . The "a" axis is an axis of pseudo-hexagonal symmetry. The angle  $(011):(0\bar{1}1)$  is  $60^\circ 26'$ , and the ratio of  $b$  to  $c$  is very nearly  $\sqrt{3}:1$  or  $1:0.577$ . The crystal twins in a manner very similar to that of aragonite, three individuals interpenetrating so as to form what appears to be a simple hexagonal crystal.

\* S. Nishikawa, 'Proc. Tokyo Math. Phys. Soc.' (1914).

† W. H. Bragg, 'Phil. Mag.', vol. 31, p. 305 (1915).

‡ R. W. G. Wyckoff, 'Jour. Amer. Chem. Soc.', vol. 44, p. 1994 ( $\text{Ag}_2\text{MoO}_4$ ) (1922). R. G. Dickinson, same journal, vol. 44, p. 774 ( $\text{K}_2\text{Zn}(\text{CN})_4$  and other crystals) (1922).

The examination of the structure is interesting for two reasons. Firstly, it is curious that it shows such contrast to that of a spinel. Secondly, the axial ratios are almost identical with those of the olivine group of minerals, and are nearly given by the ratio  $\sqrt{\frac{2}{3}} : 1 : \sqrt{\frac{3}{2}}$ .

$$\text{Mg}_2\text{SiO}_4 \quad a : b : c = 0.4666 : 1 : 0.5868$$

$$\text{BeAl}_2\text{O}_4 \quad a : b : c = 0.4707 : 1 : 0.5823$$

$$\sqrt{\frac{2}{3}} : 1 : \sqrt{\frac{3}{2}} = 0.4713 : 1 : 0.5773$$

The analysis of the structure described in this paper shows that a very simple reason can be assigned for this relationship between the axes. Chrysoberyl may be regarded as built of oxygen atoms in hexagonal close-packing, the beryllium and aluminium atoms apparently occupying so small a space between the oxygen atoms that they distort only slightly the dimensions of the hexagonal close-packed arrangement. A comparison of chrysoberyl with beryllium oxide,  $\text{BeO}$ , with alumina,  $\text{Al}_2\text{O}_3$ , and with spinel,  $\text{MgAl}_2\text{O}_4$ , shows that a common principle governs all four structures.

The hexagonal beryllium oxide, analysed by L. W. McKeehan,\* has been assigned a structure of the zinc oxide type. The oxygen atoms are placed in a manner which corresponds almost exactly with that characteristic of hexagonal close packing. The distance between atoms in the (0001) plane is equal to the length of the "a" axis, 2.696 Å. The "c" axis of  $\text{BeO}$  is equal to 4.394 Å, so that the ratio  $c/a$  is equal to 1.63, the ideal ratio for close packing being 1.632. From this it follows that the distance between oxygen atoms in successive (001) planes is very nearly equal to "a," the actual value being 2.690 Å. The evidence for the positions of the Be atoms is not strong because their scattering power is small compared with that of oxygen, but probably each beryllium atom is placed near the centre of a tetrahedron formed by four oxygen atoms, its exact position depending on a parameter which determines the shift parallel to the "c" axis, which brings the centres of the oxygen atoms into coincidence with the centres of the Be atoms.

The structure of  $\text{Al}_2\text{O}_3$  is described in 'X-rays and Crystal Structure,'† and in a paper by one of the authors‡ on birefringence. A detailed investigation by Paulings§ has established the structure more satisfactorily than was done by the author's incomplete investigation, and has given reliable values for the

\* L. W. McKeehan, 'Proc. Nat. Acad. Sci.,' vols. 8, 9, p. 270 (1922).

† 4th edition, page 181.

‡ 'Proc. Roy. Soc.,' A, vol. 106, p. 346 (1924).

§ 'Jour. Am. Chem. Soc.,' XLVII, 3, p. 781 (1925).

parameters which determine the atomic positions. One feature of the structure is of especial interest to the present argument: the oxygen atoms are very nearly in hexagonal close-packing. If each atom were displaced a distance of  $0.14\frac{1}{2}\text{\AA}$  from the position it actually occupies,\* all the atoms would lie on a lattice of the close-packed type for which  $a = 2.74\text{\AA}$ ,  $c = 4.326\text{\AA}$ ,  $c/a = 1.58$ . These figures may be compared with those already quoted for  $\text{BeO}$ ,  $a = 2.696\text{\AA}$ ,  $c = 4.384\text{\AA}$ ,  $c/a = 1.63$ . Each aluminium atom lies between six oxygen atoms, three in a plane (111) above it and three in the plane below. The aluminium atoms are displaced a distance of  $0.28\text{\AA}$  from a point halfway between the planes containing oxygen atoms in a direction parallel to the trigonal axis. The structure is illustrated in fig. 2, p. 358, of the author's paper in these Proceedings, cited above. It is shown again in fig. 1 of this paper in a simplified form, the oxygen atoms being supposed to be in a close-packed arrangement and the aluminium atoms symmetrically placed between six oxygen atoms.

In spinel,  $\text{MgAl}_2\text{O}_4$ , the oxygen atoms are very nearly in a close-packed arrangement, though in contrast to the preceding two crystals this is of the cubic (face-centred) type. Each aluminium atom lies between six oxygen atoms, and each magnesium between four oxygen atoms. If the parameter which determines the position of the oxygen atoms were given a value which brings them exactly to a cubic face-centred lattice, the distance between oxygen atoms would be  $a \times \sqrt{2}/4$ ,  $a$  being the length of the unit cube-edge containing eight molecules of  $\text{MgAl}_2\text{O}_4$ . As far as the authors are aware no exact measurement of " $a$ " for  $\text{MgAl}_2\text{O}_4$  has been published. A determination with a small crystal of spinel gave the value  $8.050\text{\AA}$  correct to one part in a thousand, the spacing being measured by finding the crystal settings for eight orders from the (111) face. The distance  $a\sqrt{2}/4$  is equal to  $2.84\text{\AA}$ .

We may summarize these features by saying that in these three structures the oxygen atoms are in positions very near to those of a close-packed arrangement, the distance between the atomic centres averaging about  $2.7\text{\AA}$  for the first two crystals and  $2.8$  for spinel. We would expect the electronic structures of the ions  $\text{Mg}^{++}$ ,  $\text{Be}^{++}$ ,  $\text{Al}^{+++}$ , to be on a much smaller scale than those of  $\text{O}^{--}$ , owing to the simpler structure of  $\text{Be}^{++}$  and the greater nuclear attraction in  $\text{Mg}^{++}$  and  $\text{Al}^{+++}$ . This makes it reasonable to consider the size and shape of the structure as principally determined in each case by the distance at which the repulsion between two oxygen ions assumes a large

\*This corresponds to assigning  $\frac{1}{4}$  to Pauling's parameter,  $u$ , which he estimates to be  $0.303 \pm 0.006$ .

value, and to take this distance as approximately equal to  $2.7 \text{ \AA}$ . The much smaller size of the metallic ions permits them to be inserted in the interstices of the oxygen arrangement where they bind together the close-packed assemblage of oxygen ions. The arrangement of these latter atoms is distorted, but its main features are preserved. If it is justifiable to regard the structures in this way, their relationship to the structure of chrysoberyl can be understood.

In fig. 1 the structures of  $\text{BeO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{MgAl}_2\text{O}_4$  are shown as close-packed

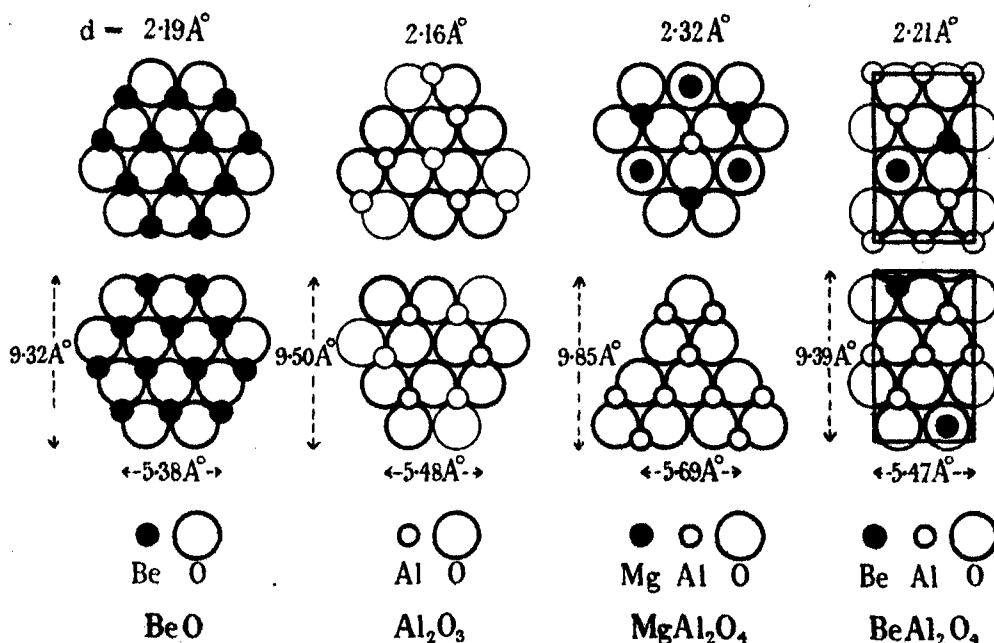


FIG. 1.—Two successive layers of oxygen atoms are shown in each case, the upper layer in the figure being supposed to be placed symmetrically on the lower layer. The distance “ $d$ ” above the figures refers to the distance between the layers. Metal ions which lie between four oxygen ions are shown as dark circles, and those which lie between six oxygen ions as light circles. In  $\text{Al}_2\text{O}_3$  groups composed of three oxygen ions with an aluminium ion above and below are distinguished by being more heavily outlined. The aluminium atoms which are lightly outlined belong to a group in an upper layer. Three oxygen atoms of a group actually approach more closely than is shown in the figure ( $2.50 \text{ \AA}$  as against  $2.74 \text{ \AA}$ ) and the two aluminium atoms are further apart ( $2.73 \text{ \AA}$  as against  $2.16 \text{ \AA}$ ). In  $\text{MgAl}_2\text{O}_4$  the magnesium atoms are on a diamond lattice. Hence two sheets of Mg atoms at a distance apart of  $1.16 \text{ \AA}$  are shown in the upper figure, whereas none occur between this layer of oxygen atoms and the one below. One-quarter of the aluminium atoms occur with the magnesium atoms, and the remainder in alternate sheets. In  $\text{BeAl}_2\text{O}_4$  half of the aluminium atoms lie between each pair of oxygen layers, forming a zig-zag row. The positions assigned to the beryllium atoms are speculative. The unit cell is outlined in the figure.

arrangements, in order that they may be compared with the structure proposed in this paper for  $\text{BeAl}_2\text{O}_4$ . The analysis of the latter crystal shows that it is built on a simple orthorhombic lattice containing four molecules of  $\text{BeAl}_2\text{O}_4$ , with dimensions  $a = 4.420 \text{ \AA}$ ,  $b = 9.390 \text{ \AA}$ ,  $c = 5.470 \text{ \AA}$ . If the close-packed hexagonal assemblage is referred to orthorhombic axes, the distance between points being  $2.7 \text{ \AA}$ , the unit cell contains four points and has dimensions

$$a = 4.41 \text{ \AA}, \quad b = 4.68 \text{ \AA}, \quad c = 2.70 \text{ \AA}.$$

In  $\text{BeAl}_2\text{O}_4$  a cell whose sides are  $a$ ,  $b/2$ ,  $c/2$  contains four oxygen atoms. For such a cell

$$a = 4.420 \text{ \AA}, \quad b = 4.695 \text{ \AA}, \quad c = 2.735 \text{ \AA}.$$

The authors were led to investigate the  $\text{BeAl}_2\text{O}_4$  structure because this suggests so strongly that the oxygen atoms are in hexagonal close-packing.

The structures are represented in fig. 1 as if the distance between the centre of the oxygen atoms were constant throughout. This is, of course, not the case. In  $\text{Al}_2\text{O}_3$ , for example, each oxygen atom is surrounded by 12 other atoms in pairs, at distances  $2.50, 2.63, 2.73, 2.75, 2.87, 2.87 \text{ \AA}$ . Similarly in spinel the positions of the oxygen atoms depend on a parameter, and they will not be quite equidistant though the estimated value of the parameter makes them nearly so. Further, in the spinels the size of the magnesium, iron, or zinc ion has an influence in determining the size of the unit cell, as if these ions were large enough to expand the close-packed assemblage. We draw attention to these points to show how far it is from our intention to suggest a fixed size for oxygen  $\text{O}^{--}$  under all circumstances. We only wish to suggest that the oxygen atoms in chrysoberyl must be very nearly in hexagonal close-packing, because the number which are packed into the unit cell does not permit any less economical use of the available space.

## 2. *The Space-Group of $\text{BeAl}_2\text{O}_4$ .*

The measurements described below were made on a specimen of chrysoberyl weighing about 1 gram. The crystal was chosen because it was untwinned. Natural faces (100) were well developed, with striations on them which gave the direction of the "c" axis. Faces (010) (001) (011) and (120) were ground on the crystal, each being about 5 mm. by 2 mm. Observations were made with the spectrometer and by photographs taken with a rotating crystal in the manner employed by Schiebold. The latter showed that the axes  $a, b, c$  of the unit cell had approximately the values  $4.41, 9.39, 5.47 \text{ \AA}$  respectively. An accurate determination of the spacings of the planes (100) (010) and (001)

was made with the ionization spectrometer. The crystal was mounted with a pinakoid plane vertical and lying in the axis of rotation. The ionization chamber was placed so as to receive one of the orders of reflexion, and its slits opened wide. The crystal is highly perfect, so that the crystal setting for which reflexion takes place can be measured to one or two minutes by rotating the crystal a few minutes at a time, and observing the strength of the reflected beam. The  $K_{\alpha}$  and  $K_{\alpha'}$  lines of rhodium are widely resolved in the higher orders (see fig. 3). Measurements on even orders up to the eighth on the face (100) and up to the twelfth on the faces (010) and (001) gave the following values for the axes

$$a = 4.420, \quad b = 9.390, \quad c = 5.470.$$

The probable error of measurement is one part in a thousand.

The perfection of the crystal was remarkable, for no broadening of the lines due to irregular orientation of the crystal planes could be detected.

Calculation shows that the unit cell  $abc$  contains four molecules of  $\text{BeAl}_2\text{O}_4$ . This gives a value for the density of 3.710, the density quoted by Groth being 3.60-3.86.

The "Schiebold" method was employed for obtaining photographs with a rotating crystal. The crystal was mounted so that a pinakoid face lay on the axis of rotation, which coincided with one of the crystallographic axes. It was rotated through about  $30^\circ$ , starting from a position where the X-rays were parallel to the face. The reflected rays were recorded on a photographic plate, placed at right angles to the incident X-ray beam at a distance of 3.54 cm. from the axis of rotation. This distance was measured by taking a photograph with a crystal of rock-salt and measuring the distance between the orders in the principal spectra of the (100) face. Two photographs were taken with each pinakoid face of chrysoberyl, the two crystallographic axes parallel to the face being set up in turn as axes of rotation. The following reflexions were observed.

Numerous measurements were made with the spectrometer to check these results. Particular attention was paid to a search for spectra, the absence of which was significant in determining the space group. In doing this, the crystal was rotated through the angle at which reflexion might be expected to take place, the chamber slits being wide so as to receive any reflected peak. The sensitivity of this test is considerable. For instance, the reflexion (004) gave a deflexion in the electrometer of 600 divisions in 3 seconds. A peak corresponding to a deflection of two or three divisions can be detected. The method employed is described in paragraph 5.



Table I.—Results of Rotating-Crystal Photographs.

	Face (100), axis [010].	Face (100), axis [001].
Very strong	(240), (400), (462)	(400)
Strong	(110), (330), (331), (392), (510), (530), (552)	(113), (312), (322), (334), (422), (513)
Moderate	(210), (310), (340), (440)	(101), (310), (311), (321), (510), (511)
Weak	(200), (261), (350)	(200), (320), (344)
	Face (010), axis [100]	Face (010), axis [001]
Very strong	(130), (140), (331), (462)	(062), (134), (192)
Strong	(170), (111.0), (280), (392)	(041), (061), (144), (174), (284)
Moderate	(040), (180), (281), (2.10.0), (2.10.2), (351)	(040)
Weak	(020), (080), (110), (370)	(020), (080), (180)
Very weak	(150), (341)	(021), (063), (0.10.1), (154), (184)
	Face (001), axis [100]	Face (001), axis [010]
Very strong	(004), (322)	(004)
Strong	(113), (333)	(022), (144), (174), (226)
Moderate	(103), (114)	(126)
Weak	(002), (105), (206), (334), (335), (344)	(002), (043), (115), (116), (184), (284)
Very weak	(101), (135), (213)	(021), (023)

Table II.—Reflexions Examined with Ionization Spectrometer.

Present.	Absent.
Pinakoids— (200), (400), (600), (800) (020), (040) (060), (080), (0.10.0), (0.12.0), (0.14.0), (0.16.0) (002), (004), (006), (008), (0.0.12)	(100), (300), (500), (700), (900) (010), (030), (050), (070), (090), (0.11.0) (001), (003), (005), (007), (009), (0.0.10)
Prisms— (021), (022), (023), (024), (025), (026) (041), (042), (043), (044), (048) (061), (062), (063), (065), (066) (081), (082), (084), (085) (0.10.1), (0.10.5) (0.12.2), (0.12.3), (0.12.4)  (101), (103), (105) (202), (204), (208) (303) (404), (408), (4.0.12) (505)  (110), (120), (130), (140), (150), (160), (170), (180), (190), (1.10.0), (1.11.0) (210), (220), (230), (240), (260), (270), (280), (2.10.0) (310), (320), (330), (340), (350), (360), (370), (390), (3.15.0) (440), (480), (4.12.0) (510)	(011), (012), (031), (033), (051), (055), (071)          (102), (104), (201), (306), (401), (601), (603)

These results may be summarized as follows :—

Pyramid faces of all types are present. The crystal is, therefore, built on a simple orthorhombic space lattice whose axes are  $a=4.420$  Å,  $b=9.390$  Å,  $c=5.470$  Å.

Planes of the type  $(okl)$  have their spacings halved when  $k$  is odd.

Planes of the type  $(hol)$  have their spacings halved when  $(h+l)$  is odd.

All planes of the type  $(hko)$  have normal spacings.

As special cases of the above rules, all pinakoid spacings are halved.

If we assume that the crystal is holohedral, the space group must be  $V_h^{16}$ , as may be seen by consulting the tables of Niggli, Wyckoff, or Astbury and Yardley. Taking as origin a centre of symmetry of the structure at the centre of the unit cell the elements of symmetry have the following positions.

Reflexion planes.	$(001)_\frac{1}{2}$	$(001)_{-\frac{1}{2}}$	
Glide planes.	$(100)_\frac{1}{2}$	$(100)_{-\frac{1}{2}}$	translation $b/2$
Glide planes.	$(010)_\frac{1}{2}$	$(010)_{-\frac{1}{2}}$	translation $a/2, c/2$ .

Symmetry centres I.  $(000), (00\frac{1}{2}), (\frac{1}{2}\frac{1}{2}0), (\frac{1}{2}\frac{1}{2}\frac{1}{2})$ .

II.  $(\frac{1}{2}00), (\frac{1}{2}0\frac{1}{2}), (0\frac{1}{2}0), (0\frac{1}{2}\frac{1}{2})$ .

Digonal screw axes exist parallel to  $a, b$  and  $c$ , the positions of which are shown in fig. 4.

An atom whose co-ordinates with reference to the origin are  $x, y, z$  is converted by the operation of the elements of symmetry into eight atoms within the unit cell.

$$\begin{aligned} \pm (x, y, z), \quad \pm \left( -\frac{a}{2} + x, \frac{b}{2} - y, -z \right), \\ \left( x, y, \frac{c}{2} - z \right), \quad \pm \left( -\frac{a}{2} + x, \frac{b}{2} - y, -\frac{c}{2} + z \right). \end{aligned}$$

Let the amplitude due to a given atom be  $A$ , when reflexion in the  $hkl$  plane is taking place. The eight corresponding atoms contribute a wave whose amplitude is given by the expression

$$8A \cos \left\{ (h+k) \frac{\pi}{2} + h\alpha \right\} \cos \left\{ (h+k+l) \frac{\pi}{2} + k\beta \right\} \cos \left( \frac{l\pi}{2} + l\gamma \right) \cos (h+k+l)\pi,$$

where

$$\alpha = 2\pi \frac{x}{a}, \quad \beta = 2\pi \frac{y}{b}, \quad \gamma = \frac{2\pi z}{c}.$$

The form of the expression shows that the resultant amplitude is zero when  $k$  is zero and  $(h + l)$  is odd, or when  $h$  is zero and  $k$  is odd. The factor  $\cos (h + k + l) \pi$  affects only the sign of the expression, and may be neglected in calculating the structure factor for a given plane  $(hkl)$  as it affects all atoms equally.

### 3. The Arrangement of the Atoms.

The arrangement of the atoms in the unit cell must be deduced from the relative intensities of the spectra. The beryllium atoms are very light, and their scattering power is small compared with that of the oxygen and aluminium atoms. They will be neglected altogether for the present.

An examination of the spectra gives a very suggestive hint as to the structure. With few exceptions, *those spectra are very strong which correspond to reflexion by the hexagonal close-packed lattice.*

In fig. 2 that part of the hexagonal close-packed assemblage is shown which corresponds to the unit cell of chrysoberyl. The circles and crosses represent two successive layers of oxygen atoms.

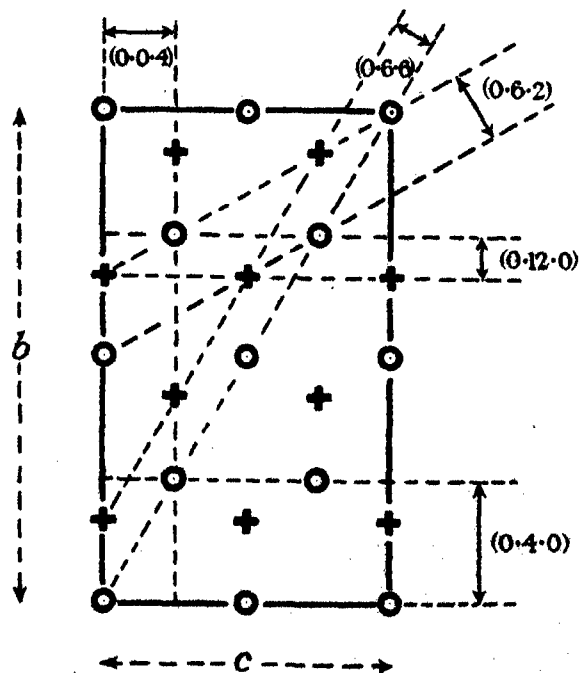


FIG. 2.—Planes of the hexagonal close-packed assemblage referred to the orthorhombic axes of  $\text{BeAl}_2\text{O}_4$ .

Fig. 3 shows the reflexion from the (001) face. Owing to the space-group requirements even spectra alone are present. Reflexions (004), (008), (0012)

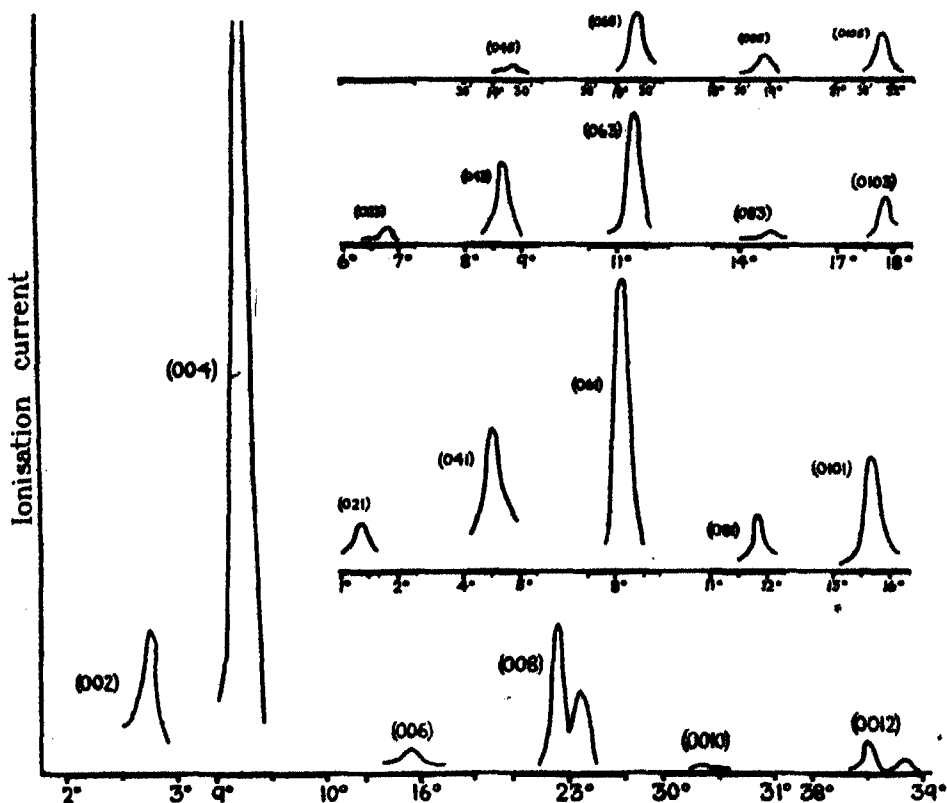


FIG. 3.—Reflexions from the face (001) and from other faces of  $\text{BeAl}_2\text{O}_4$ .  
Horizontal Scales represent Crystal Angle (zero error,  $-3^\circ 42'$ ).

are very strong, and (002), (006), (0.0.10) are comparatively very weak. This can only be due to a distribution of the diffracting matter in four sheets parallel to (001). A comparison with fig. 2 shows that this is to be expected from the close-packed assemblage whose existence we are trying to prove.

The reflexions from the face (010) have the following relative intensities :—

(020)	(040)	(060)	(080)	(0.10.0)	(0.12.0)	(0.14.0)
6.3	19.6	2.1	6.7	—	17.4	6.2

This again is in agreement with the close-packed structure. The exceptionally strong spectrum is (0.12.0), for which all the oxygen atoms are in phase.

Reflexions (020) and (060) are weak, while (040) and (080) are moderately strong. Further, (066) is extremely strong, being about equal to (040), and (062) is also one of the strongest spectra yielded by the crystal. These planes are marked in fig. 2, and it will be seen that they receive a strong contribution from all the points.

The authors examined a large number of planes with the same result. The close-packed oxygen atoms may be regarded as lying on two interpenetrating orthorhombic lattices whose axes are  $a$ ,  $b/2$ ,  $c/2$ . The face with sides  $b/2$ ,  $c/2$  is centred. The plane whose indices are  $(hkl)$  only receives a contribution to its structure factors from these atoms if  $k$  is even,  $l$  is even, and  $(k + l)/2$  is even. A survey of the reflected spots in the photographs shows that all planes whose indices obey these conditions do in fact give strong reflexions. Examples are 144, 284, 322, 462, 184, 140, 240, 404.

This supports the indication given by the dimensions of the unit cell, that the oxygen atoms are approximately in hexagonal close-packing. We must now try (a) whether this arrangement is consistent with the space group, (b) whether the aluminium atoms can be so placed that the relative intensities of the spectra can be satisfactorily explained.

Trial shows that there is only one way of placing the close-packed assemblage with reference to the symmetry elements of the space group. This is shown in fig. 4. The oxygen atoms are represented by circles and crosses as before. The crosses are at a height  $a/4$  from the bottom of the unit cell, the circles at a height  $3a/4$ . The screw axes parallel to  $c$  are at heights  $0$ ,  $a/2$ ,  $a$ , and those parallel to  $b$  at heights  $a/4$ ,  $3a/4$ . Glide planes parallel to (100) with translation  $b/2$ , exists at heights  $a/4$ ,  $3a/4$ .

The positions of the aluminium atoms can be found by comparing the intensities of reflexion of the more important planes. The spectra from the faces (100), (010), (001), (120), (011) were measured in terms of the reflexion (400) from rocksalt, these faces having been ground on the crystal. The crystal was turned with a uniform angular velocity and the integrated reflexion measured, especial care being necessary to see that the whole of the X-ray beam fell on the very small crystal face. The results are given below (see Table III), the integrated reflexions from NaCl (400) being put equal to 100.

The unit cell contains eight aluminium atoms. In the general case, a point in the cell is multiplied into eight by the symmetry operations. It is therefore possible for all the aluminium atoms to be equivalent, and to lie in positions determined by three parameters. Alternatively, they may lie on symmetry planes or at symmetry centres. In both these cases there are four equivalent

points in the cell, so the aluminium atoms would form two groups of four. The spectra from the face (001) shown in fig. 3 are by themselves almost conclusive evidence that the aluminium atoms are divided into two kinds, four of them lying at symmetry centres and four on reflexion planes. This conclusion has, of course, been checked by an examination of a very large number of reflexions,

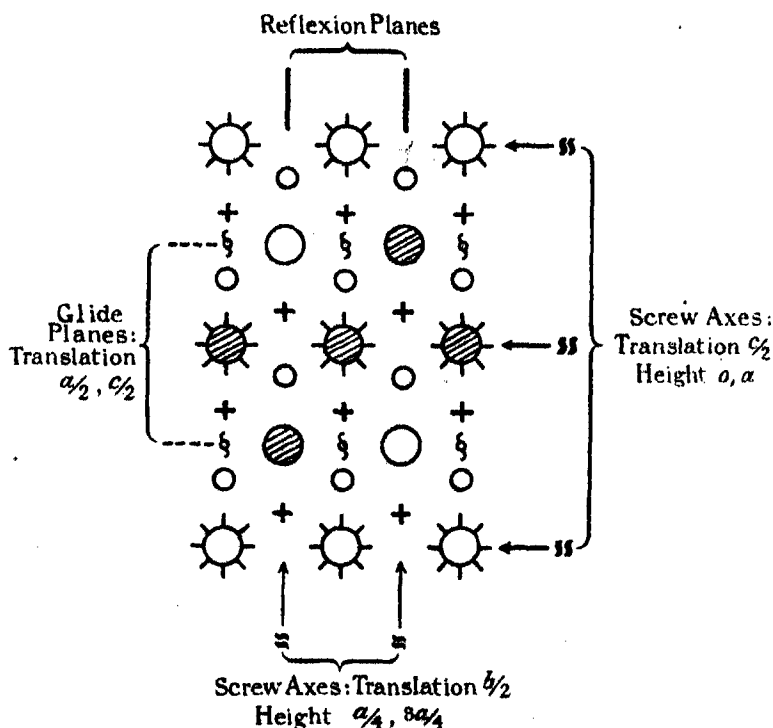
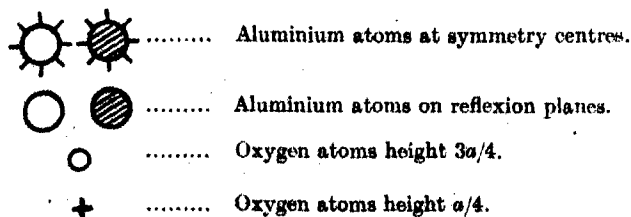


FIG. 4.—Approximate positions of aluminium and oxygen atoms in  $\text{BeAl}_2\text{O}_4$  and symmetry elements of the structure.



but it would be lengthy to recount all the evidence, and the following will serve as an example of its nature. The great strength of the reflexions (004), (008), (0.0.12) and the weakness of (002), (006), (0.0.10) can only mean that the diffracting material is gathered into sheets at intervals  $c/4$  very nearly equal in

Table III.—Integrated Reflexion from Faces of  $\text{BeAl}_2\text{O}_4$ , Expressed as Percentages of  $\text{NaCl}$  (400).

Indices.	$\sin \theta$ .	Integrated Reflexion.	Structure Factor. (Idealised Structure.)	Structure Factor. (Modified Structure.) $\theta_1 = 0^\circ, \theta_2 = 10^\circ$ .
(022)	0.1299	26.0	$\text{Al}_2 - \text{O}_2$	$\text{Al}_{1.2} - \text{O}_2$
(040)	0.1308	19.6	$\text{Al}_2 - \text{O}_2$	$\text{Al}_{1.2} - \text{O}_2$
(200)	0.1392	6.4	$\text{Al}_2 - \text{O}_4$	$\text{Al}_2 - \text{O}_4$
(240)	0.1910	100.0	$\text{Al}_2 + \text{O}_4$	$\text{Al}_{1.2} + \text{O}_4$
(004)	0.2246	107.0	$\text{Al}_2 + \text{O}_4$	$\text{Al}_2 + \text{O}_4$
(044)	0.2598	11.1	$\text{Al}_2 - \text{O}_2$	$\text{Al}_{1.2} - \text{O}_2$
(080)	0.2616	6.7	$\text{Al}_2 - \text{O}_2$	$\text{Al}_{1.2} - \text{O}_2$
(400)	0.2784	61.5	$\text{Al}_2 + \text{O}_4$	$\text{Al}_2 + \text{O}_4$
(006)	0.3897	18.0	$\text{Al}_2 + \text{O}_4$	$\text{Al}_{1.2} + \text{O}_4$
(0.12.0)	0.3924	17.4	$\text{Al}_2 + \text{O}_4$	$\text{Al}_{0.5} + \text{O}_4$
(000)	0.4176	1.3	$\text{Al}_2 - \text{O}_4$	$\text{Al}_2 - \text{O}_4$
(008)	0.4492	16.5	$\text{Al}_2 + \text{O}_4$	$\text{Al}_2 + \text{O}_4$
(800)	0.5568	3.0	$\text{Al}_2 + \text{O}_4$	$\text{Al}_2 + \text{O}_4$
(0.0.12)	0.6738	3.0	$\text{Al}_2 + \text{O}_4$	$\text{Al}_2 + \text{O}_4$

scattering power. If the eight aluminium atoms are in the general position and are equivalent, they occur in pairs imaged in the reflecting planes (fig. 4). To explain the very strong reflexion (004) they must lie nearly in the same planes as the oxygen atoms parallel to (001). This involves a position distant  $c/4$  from the reflecting plane, since the only alternative is that they should be very close together, which is highly improbable. Such an arrangement would place all the aluminium atoms on sheets (001) halfway between the reflexion planes, and this would give a very strong second order. Actually the second order is extremely weak. A similar argument rules out an arrangement of the aluminium atoms in two sets of four on the reflecting planes, and an arrangement in two sets of four at the symmetry centres, as both would also result in a strong second order.

*The aluminium atoms must be of two kinds. Four atoms in the unit cell are at centres of symmetry, and four lie on the reflexion planes.* This arrangement explains in a natural manner the very striking distribution of intensity in the (001) spectra. All atoms combine in the structure factors for (004), (008), (0.0.12). The effect of the four Be atoms, and of distortion of the close-packed oxygen arrangement, is alone responsible for (002), (006), (0.0.10), which are consequently very weak.

The aluminium atoms at the symmetry centres have no degrees of freedom. It is interesting to find atoms of this type in a structure of orthorhombic symmetry. The atoms are marked in the figure by circles with rays. Their

positions are  $(000)$ ,  $(00\frac{1}{2})$ ,  $(\frac{1}{2}\frac{1}{2}0)$ ,  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ , and others due to translations of the lattice. The shaded circles are at a height  $a/2$ , the plain circles at heights zero and  $a$  from the bottom of the cell.

The approximate position of the aluminium atoms which lie on the reflexion planes can be ascertained by similar reasoning. For example, the reflexions from the  $(100)$  face are alternately weak and strong

200	400	600	800
6.4	61.5	1.3	3.0

The oxygen atoms contribute an amount  $O_4$  to the structure factor for all these reflexions. The reflexion  $(200)$  is very weak considering its small glancing angle and the two aluminium atoms must be almost opposite in phase to the four oxygen atoms. This suggests that the aluminium atoms of the second type, like those at the symmetry centres, lie halfway between the oxygen  $(100)$  planes, or that the  $x$  co-ordinate of the typical atom, referred to the centre of the cell as origin, is nearly zero.  $(020)$  is very weak, hence the  $y$  co-ordinate of the Al atom, cannot be far from  $b/4$  (see fig. 4). These two co-ordinates fix the atoms since we know that  $z$  is equal to  $c/4$ . The four atoms lie nearly at the centre of six oxygen atoms, three above and three below, in the positions marked in fig. 4. Their positions are defined by two parameters. Since one parameter is nearly equal to  $\frac{1}{2}\pi$ , it is easier in the subsequent analysis to call these parameters  $\theta_1$  and  $\frac{1}{2}\pi + \theta_2$ , where  $\theta_1 = 2\pi(x/a)$ ,  $\frac{1}{2}\pi + \theta_2 = 2\pi(y/b)$ . In the fourth column of Table III the contributions of the Al and O atoms to the reflected amplitudes are set down  $\theta_1$  and  $\theta_2$ , being supposed to be zero, in order to show that the relative intensities of the most important spectra are explained by this simple arrangement. In the last column the factors for a value of  $\theta_2$  equal to  $10^\circ$  are given, this value giving a closer correspondence.

#### 4. Method of Analysis.

The intensities of the spots in the photographs, and the ionization measurements of reflexion, provide a mass of material with which to test the structure suggested by this preliminary investigation, and to find what displacements consistent with the symmetry must be given to the atoms to get the best agreement. One aluminium atom of the  $\text{BeAl}_2\text{O}_4$  molecule is fixed in position. The other aluminium has two parameters, two oxygen atoms on the reflexion planes have two parameters each, and the remaining two equivalent oxygen atoms are fixed by three parameters. The beryllium atom has



either two parameters or none, as it may lie on a reflexion plane or at a symmetry centre. Therefore at least nine, possibly eleven, parameters have to be fixed in order to determine the structure if we proceed in a formal manner. The present analysis does not pretend to do this, for the problem is too complex for the data we have obtained. We proceeded as follows. On the analogy of the  $\text{Al}_2\text{O}_3$  structure, we supposed that the displacement of the oxygen atoms from close-packed positions is not greater than 0.1 to 0.2 Å. Such a displacement hardly affects the structure factor for planes where  $h, k, l$  are not large. The aluminium atoms may be expected to have a larger shift, and as they are heavier this shift is of greater importance. We therefore carried out the comparison in three stages.

(a) The idealised structure (where the oxygen atoms are in the exact positions of hexagonal close-packing, and each aluminium atom exactly at the centre of six oxygen atoms) was tested to see whether it explained the general features of all the photographs and spectrometer results. This was found to be the case for small values of  $h, k, l$ .

(b) The aluminium atoms on the reflexion planes were supposed to be displaced to positions  $\theta_1, \frac{1}{2}\pi + \theta_2$ , and the oxygens to remain in the close-packed positions;  $\theta_1$  and  $\theta_2$  were determined by a comparison of certain intensities.

(c) This structure was then tested, and gave a remarkably complete explanation of all our observations, both photographic and spectrometric.

### 5. *Observations of Intensity of Reflexion.*

The absolute measurements of intensity for certain important faces have already been described. The other observations were qualitative.

The spots on the photographic plates give an approximate idea of the relative intensity of reflexion by the different planes. The absence of certain reflexions, permitted by the space group, is as significant as the relative strength of those which do appear. It is therefore important to make a table of those reflexions which can appear in each rotating-crystal photograph, so as to see which are missing. The number of reflexions is limited by the angle through which the crystal is rotated, for only those planes are represented which pass through the reflecting position while the crystal is turning through  $30^\circ$ . In the present case, another limitation came in which we did not realize at first till we noticed that certain reflexions, known otherwise to be strong, were absent from photographs where the planes had been turned through the reflecting position. We used ground-crystal faces of extended area, parallel to the pinakoids. The beam of X-rays fell on the centre of the face and was reflected by a plane such

as  $(h, k, l)$ . If the beam after reflexion passes out of the face again, a spot is produced. If, however, it continues after reflexion to be inside the crystal, it is completely absorbed. Let us suppose that the " $a$ " axis of the crystal is the vertical axis of rotation, and that we are reflecting from the " $b$ " face (010). Many of the spots will be formed by planes  $(h, k, o)$ . The condition that the reflected ray shall pass out in front of the face (010), and not behind it, is that  $k/b$  shall be greater than  $h/a$ , or that the plane  $(h, k, o)$  shall make an angle of less than  $45^\circ$  with the vertical. For instance, in chrysoberyl " $b$ " is more than twice as great as " $a$ ." When rotating the " $b$ " face about the " $a$ " axis the plane (240) cannot give a spot on the diagram, although it reflects extremely strongly, for the plane makes an angle of  $46^\circ 44'$  with the vertical. When reflecting from the " $a$ " face, with the " $b$ " axis of rotation, (240) gives one of the most intense spots in the photograph, since it only makes an angle of  $43^\circ 16'$  with the vertical. Similar restrictions apply to planes  $(h, k, l)$  of all types. These limitations do not exist if the crystal is small and is bathed in X-rays.

The reflexions observed in the photographs are given in Table I. A complete analysis of a photograph, comparing the number of reflexions observed with the total number which are possible, is given in Section 8.

The ionization spectrometer was used to make a survey of a large number of reflexions very like that given by a rotating-crystal photograph. The method was practically identical with that which has been used by W. H. Bragg for the examination of small transparent crystals of organic substances ('X-Rays and Crystal Structure,' p. 20, 4th edition). Certain modifications had to be introduced in the present case because the crystal was large and absorbed the radiation considerably. The crystal was mounted on a holder similar to that of a three-circle goniometer. The holder is shown in fig. 5.

Suppose that it is desired to examine a set of planes  $(h, k, o)$ . The crystal is placed on the holder so that the face (010) is perpendicular to the plane of the large vertical circle A, and contains the vertical axis of the spectrometer about which the holder turns. The small vertical circle B is rotated until the " $c$ " axis is horizontal and the " $a$ " axis vertical. These adjustments are made by a combination of optical and X-ray reflexions. Then, by rotating the circle A, any plane  $(h, k, o)$  can be brought into a vertical position. The X-rays still fall on the crystal face when it is inclined because they pass through the exact centre of the circle A. The ionization chamber is set for the various orders of reflexion from the plane  $(h, k, o)$  in turn, and the crystal moved by five minutes at a time through the reflecting angle. The ionization currents

are plotted, and the peak on the curve gives an estimate of the intensity of reflexion. In this way a rapid survey of a large number of reflexions can be made. A set of observations lasting a few seconds each and extending over a degree are sufficient to plot a reflexion peak. The curves in fig. 3 illustrate the method, which has certain advantages over the photographic method. When once the crystal has been correctly oriented on the holder, the observed glancing angle of reflexion for any plane checks with the calculated angle to within a few minutes. There is therefore little danger of one reflexion being mistaken for another. In the rotating-crystal photographs this is sometimes difficult to avoid, for two planes with different indices will give spots in almost identical positions on the photographic plate. The ionization method tells

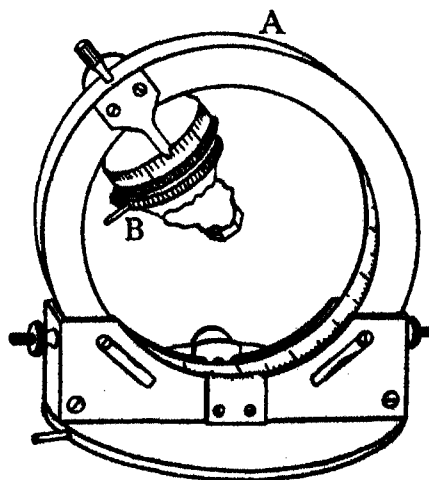


FIG. 5.—Crystal holder for rapid survey of reflexion with ionization spectrometer.

accurately the angle at which the crystal is set, as well as the angle at which the chamber is set, for each reflexion, and this gives its origin in nearly every case. A combination of the two methods, photographic and spectrometric, obviates all doubt.

In the observations tabulated below, no precautions were taken to see that the whole beam of X-rays fell on the crystal face. As the face is inclined more and more to the vertical, the strength of reflexion falls away because absorption is greater and because the rays miss the crystal to a greater extent. The recorded intensities are therefore influenced by continuous factors which vary widely, and make it only possible to compare peaks whose indices are nearly the same.

The relative intensities of the reflexions ( $h, k, o$ ), for example, depend on whether we are using the face (100) or (010).

Our examination was confined to the prism faces. The figure set down for each reflexion represents the difference between the peak ionization current, and the general current due to white radiation and natural leak when the crystal is not set at the reflecting position.

Table IV.—Survey of Reflexions with the Spectrometer. Planes marked (?) are those for which a very small reflexion has been observed.

Planes ( <i>o k l</i> ). <i>k</i> even.						
Face (010)						
<i>k</i> =	2	4	6	8	10	12
<i>l</i> = 1	30	66	175	30	60	
2	70	12	280	45	—	20
3	6	48	120	?	25	30
4		60		30		35
5		?	36	12	25	
6			105			

Face (001)						
<i>k</i> =	2	4	6	8	10	12
<i>l</i> = 1						
2	235	12				
3	53	140	150			
4	30	180		40		
5	18	15	115	?	35	
6	155	?	260			
7	?					
8		20				

Planes ( $h \ 0 \ l$ ).  $h + l$  even.

[illegible]

Table IV—(continued).

Planes ( $h k o$ ). No conditions.

		Face (100)													
$k =$		1	2	3	4										
$h = 1$		270	23	162	162										
	2	58	?	27	333										
	3	69	?	196	124										
	4	3	?	?	89										
	5	44	18	52	25										
	6	12	?	?	59										
	7	14	?	16	11										
	8	?	?	?	7										

		Face (010)											
$k =$		1	2	3	4	5	6	7	8	9	10	11	12
$h = 1$		82	35	470	654	72	52	353	140	4	2	102	
	2		?	?	590	—	?	21	252		90		
	3			90	27	16	12	170		?			
	4				43				21				30
		Also 0.15.3 .... 22											

#### 6. Comparison of Observed Reflexions with Structure Factors of the Idealized Structure.

The proposed structure of chrysoberyl, projected on the planes  $bc$ ,  $ac$ , and  $ab$ , is shown in fig. 6. The oxygen atoms are in hexagonal close-packing. The aluminium atoms are placed in the positions of highest symmetry (idealized structure), while the arrows show the directions in which displacements  $\theta_1$  and  $\theta_2$  consistent with the symmetry can be made.

If we take the idealized structure in the first place, neglecting the beryllium atoms, the following rules give the structure factors for the different planes:—

Planes (*o*, *k*, *l*).

(022) $\text{Al}_2 - \text{O}_2$	(044) $\text{Al}_2 - \text{O}_2$	(062) $\text{Al}_2 + \text{O}_4$	(084) $\text{Al}_2 - \text{O}_2$
(026) $\text{Al}_2 - \text{O}_2$	(048) $\text{Al}_2 - \text{O}_2$	(066) $\text{Al}_2 + \text{O}_4$	(088) $\text{Al}_2 - \text{O}_2$
(0.2.10) $\text{Al}_2 - \text{O}_2$	(0.4.12) $\text{Al}_2 - \text{O}_2$	(0.6.10) $\text{Al}_2 + \text{O}_4$	(0.8.12) $\text{Al}_2 - \text{O}_2$

All other planes have a zero structure factor.

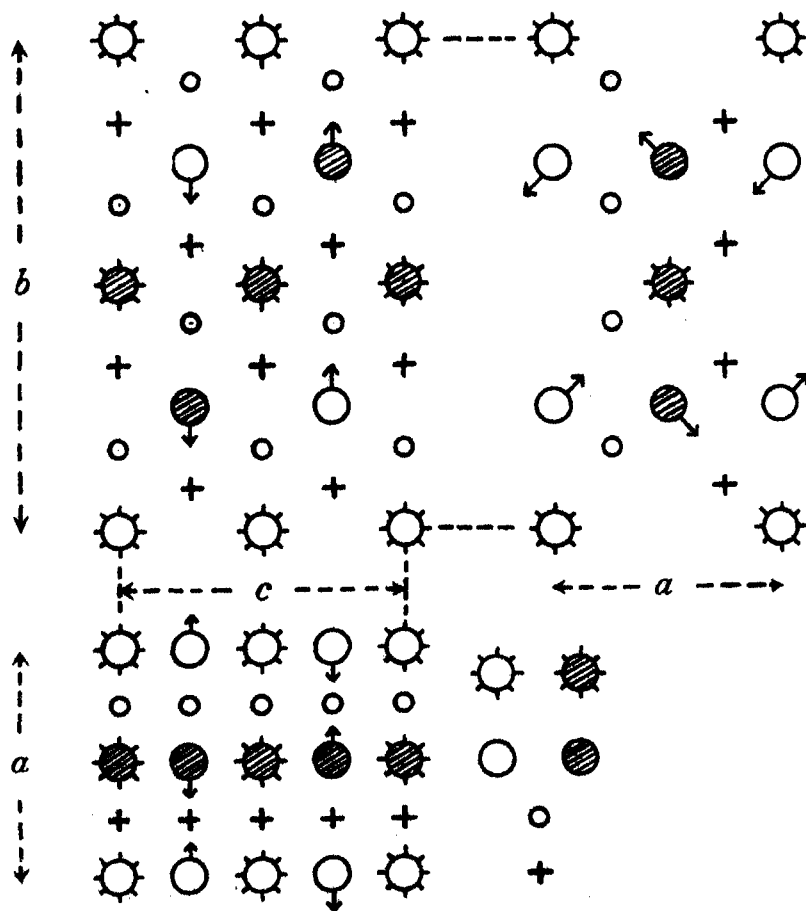


FIG. 8.—Projection of structure of  $\text{BeAl}_2\text{O}_4$  on principal planes.

Comparing this with the figures in Table VI, it will be seen that (022), (026), (044), (062), (066) are, in fact, all very strong reflexions, due consideration being paid to their positions in the table.\* It is clear, however, that the simple

\* For example (022) is weak when the face (010) is being used, because this face has to be tilted to a very large angle with the vertical. When the face (001) is used the strength of (022) is apparent.

structure does not explain the large size of (041), (043), (061), (063), (065). This, as will be seen, is due to the fact that  $\theta_2$  is not equal to zero.

*Planes (h, o, l).*

The rules for the structure factors of the idealized structure are very simple, corresponding to the simple arrangement of diffracting points shown in fig. 6:—

$$\begin{array}{ll} (404), (408), (804), (808), \text{ etc.} & \dots\dots\dots \text{Al}_2 + \text{O}_4 \\ (204), (208), (604), (608) & \dots\dots\dots \text{Al}_2 - \text{O}_4 \end{array}$$

All other planes have a zero structure factor.

This agrees with the results in Table IV. All the reflexions are very weak with the exception of 404, 408, 804. To this list should be added the very strong reflexions 400, 800, 004, 008, 0012. The whole set proves that the projection on the "ac" plane in fig. 6 is very near the truth, and that  $\theta_1$  cannot be large.

*Planes (h, k, o).*

The conditions here are more complicated, and it is simplest to give a list of structure factors:—

(110) Al	(210) —	(310) Al	(410) —
(120) —	(220) —	(320) —	(420) —
(130) Al	(230) —	(330) Al	(430) —
(140) $\text{O}_4 \cos 30^\circ$	(240) $\text{Al}_2 + \text{O}_2$	(340) $\text{O}_4 \cos 30^\circ$	(440) $\text{Al}_2 - \text{O}_2$
(150) Al	(250) —	(350) Al	(450) —
(160) —	(260) —	(360) —	(460) —
(170) Al	(270) —	(370) Al	(470) —
(180) $\text{O}_4 \cos 30^\circ$	(280) $\text{Al}_2 + \text{O}_2$	(380) $\text{O}_4 \cos 30^\circ$	(480) $\text{Al}_2 - \text{O}_2$

There is a general agreement with Table IV. Amongst the planes (2ko), for example, (240) and (280) stand out in the most striking fashion, and so also does (440) in the row (4ko). The failure of the simple structure to explain the facts is evident in cases such as the set of reflexions (110) to (1.11.0). The planes (110), (130), (150), (170), (190), (1.11.0) have identical structure factors, but their intensities of reflexion as measured by setting the face (010) on the holder are in the ratio 82, 470, 72, 353, 4, 102. The very small value for (110) is due to the extreme tilt of the crystal in this case, and (110) measured by setting up the (100) face on the holder is quite large. It is clear, however, that the other reflexions are alternately strong and weak instead of falling off evenly.

## 7. Determination of the Parameters.

The set of reflexions which have just been mentioned above provide a ready means of determining  $\theta_2$ , the displacement of the aluminium atom parallel to the "b" axis. Introducing displacements  $\theta_1$  and  $\theta_2$  into the simple structure, the structure factors\* have the following values :—

Plane.	Structure factor.	Observed intensity.	Plane.	Structure factor.	Observed intensity.
110	$\text{Al}(1 - \cos \theta_1 \sin \theta_2)$	82	310	$\text{Al}(1 - \cos 3\theta_1 \sin \theta_2)$	—
130	$\text{Al}(1 + \cos \theta_1 \sin 3\theta_2)$	470	330	$\text{Al}(1 + \cos 3\theta_1 \sin 3\theta_2)$	90
150	$\text{Al}(1 - \cos \theta_1 \sin 5\theta_2)$	72	350	$\text{Al}(1 - \cos 3\theta_1 \sin 5\theta_2)$	16
170	$\text{Al}(1 + \cos \theta_1 \sin 7\theta_2)$	353	370	$\text{Al}(1 + \cos 3\theta_1 \sin 7\theta_2)$	170
190	$\text{Al}(1 - \cos \theta_1 \sin 9\theta_2)$	4	390	$\text{Al}(1 - \cos 3\theta_1 \sin 9\theta_2)$	4
1.11.0	$\text{Al}(1 + \cos \theta_1 \sin 10\theta_2)$	102	—	—	—

An examination of other sets of spectra show that  $\theta_1$  is small, and therefore  $\cos \theta_1$  is very nearly unity. It is clear that  $\theta_2$  must be positive, since (130), (170) are large and (150) is small. In order to explain the very small values of (190), (390),  $\theta_2$  must be nearly equal to  $\pi/18$  ( $10^\circ$ ). The structure factors for (190) and (390) are then small. This estimate of  $\theta_2$  is confirmed by other series of spectra. The following appear on one of the rotating-crystal photographs.

Plane.	Structure factor.	Observed intensity.
134	$\text{Al}(1 + \cos \theta_1 \sin 3\theta_2)$	Very strong.
144	$-\text{Al}(\sin \theta_1 \sin 4\theta_2) + \text{O}_4 \cos \pi/6$	Very strong.
154	$\text{Al}(1 - \cos \theta_1 \sin 5\theta_2)$	Weak.
164	$\text{Al}(\sin \theta_1 \sin 6\theta_2)$	Very weak.
174	$\text{Al}(1 + \cos \theta_1 \sin 7\theta_2)$	Strong.
184	$-\text{Al}(\sin \theta_1 \sin 8\theta_2) + \text{O}_4 \cos \pi/6$	Weak.
194	$\text{Al}(1 - \cos \theta_1 \sin 9\theta_2)$	Absent.

A value of  $\pi/18$  for  $\theta_2$  explains these results.

The sets of planes (021) . . . (0.10.1), (023) . . . (0.10.3), (025) . . . (0.10.5) whose reflexions are plotted in fig. 3 are interesting. The structure factor for the aluminium atoms lying in the reflexion planes are :—

021, 023, 025	$\text{Al} \sin 2\theta_2$ .
041, 043, 045	$\text{Al} \sin 4\theta_2$ .
061, 063, 065	$\text{Al} \sin 6\theta_2$ .
etc.	etc.

\* Formulas for the structure factors are given in Section 9.



The aluminium atoms at symmetry centres make no contribution. The oxygens only contribute in so far as they are displaced from close packing. All atoms lying on the reflexion planes contribute amounts to the structure factor for (*okl*) which only depend on *k*, and not on *l*, when *l* is odd. We would, therefore, expect to find a very similar series of spectra in these three sets, and it is clear from the figure that this is the case. It is also clear that no value of  $\theta_2$  can explain the results completely; for instance, the weakness of reflexions (08 $\bar{l}$ ). Slight displacements of the oxygen atoms must explain this, but the problem is too complex for the present analysis.

In Table V the structure factors and observed intensities for a set of planes (*hko*) are set out in full, with the object of estimating the value of  $\theta_1$ , and of searching for an indication of the position of the beryllium atoms. The intensities were measured by oblique reflexion from the plane (100), as it is more convenient with this setting to examine planes with large values of *h*. They are again a qualitative indication of the reflecting power of the planes.

Consider in the first place the planes for which  $k = 2$ . Since  $\theta_2$  is about  $10^\circ$ ,  $\sin 2\theta_2 = 0.34$ ,  $\cos 2\theta_2 = 0.94$ . The striking feature of all these reflexions is their extreme smallness. If  $\theta_1$  were large, or if the oxygen atoms were much displaced from hexagonal close-packing, some of these planes would have an appreciable structure factor and reflexions would have been observed. Their weakness is, therefore, evidence against both these possibilities. As an estimate, based on the general correspondence of structure factor and intensity,  $\theta_1$  cannot be greater than  $5^\circ$ . The reflexions for which *h* is even and *k* odd support this conclusion. The only exception is the plane 210, which is moderate in strength, even when the small angle at which it occurs is allowed for.

If we now consider the planes for which  $k = 4$ , these all receive a strong contribution from the close-packed oxygen atoms and the effect is evident in their general strength. The contrast between these two sets for which  $k = 2$ , and  $k = 4$ , supports this arrangement of the oxygen atoms.

All planes for which *h* and *k* are odd give strong reflexions, since the aluminium atoms at the symmetry centres contribute to them.

A comparison such as this, which is typical, makes us feel confident that the structure we propose cannot be far from the truth. There are so many parameters, however, that it is impossible to fix the exact value of any one of them. It so happens that  $\theta_1$  is more difficult to determine than  $\theta_2$ , apparently because it is so small. It is even impossible to say from the set for which  $k = 4$  what is the sign of  $\theta_1$ , for the effect of the oxygen atoms swamps the contribution due to the aluminium atoms.

Table V.—Structure Factors and Observed Intensities, Planes ( $h, k, o$ ).

$k = 1.$			$k = 2.$		
	Structure Factor.	Intensity.	Structure Factor.	Intensity.	
$h = 1$	$\text{Al } (1 - \cos \theta_1 \sin \theta_2)$ $\quad \quad \quad + \text{ Be } (0.6)$	270	$-\text{Al } (\sin \theta_1 \sin 2\theta_2) + \text{Be } (0.6)$ ....	23	
2	$\text{Al } (\sin 2\theta_1 \cos \theta_2)$ $\quad \quad \quad + \text{ Be } (0.5)$	58	$\text{Al } (1 - \cos 2\theta_1 \cos 2\theta_2)$ ....	?	
3	$\text{Al } (1 - \cos 3\theta_1 \sin \theta_2)$ $\quad \quad \quad + \text{ Be } (0.6)$	69	$-\text{Al } (\sin 3\theta_1 \sin 2\theta_2) + \text{Be } (0.6)$ ....	?	
4	$\text{Al } (\sin 4\theta_1 \cos \theta_2)$	3 ?	$\text{Al } (1 - \cos 4\theta_1 \cos 2\theta_2) - \text{Be } (0.5)$	?	
5	$\text{Al } (1 - \cos 5\theta_1 \sin \theta_2)$ $\quad \quad \quad + \text{ Be } (0.6)$	44	$-\text{Al } (\sin 5\theta_1 \sin 2\theta_2) - \text{Be } (0.6)$ ....	12, 6	
6	$\text{Al } (\sin 6\theta_1 \cos \theta_2)$ $\quad \quad \quad + \text{ Be } (0.5)$	8, 4*	$\text{Al } (1 - \cos 6\theta_1 \cos 2\theta_2)$ ....	?	
7	$\text{Al } (1 - \cos 7\theta_1 \sin \theta_2)$ $\quad \quad \quad + \text{ Be } (0.6)$	10, 4	$-\text{Al } (\sin 7\theta_1 \sin 2\theta_2) - \text{Be } (0.6)$ ....	?	
8	$\text{Al } (\sin 8\theta_1 \cos \theta_2)$	?	$\text{Al } (1 - \cos 8\theta_1 \cos 2\theta_2) - \text{Be } (0.5)$	?	
$k = 3.$			$k = 4.$		
	Structure Factor.	Intensity.	Structure Factor.	Intensity.	
$h = 1$	$\text{Al } (1 + \cos \theta_1 \sin 3\theta_2)$ ....	162	$\text{Al } (\sin \theta_1 \sin 4\theta_2)$ $\quad \quad \quad - \text{Be } (0.6) - \text{O}_4 \cos \pi/6$	162	
2	$-\text{Al } (\sin 2\theta_1 \cos 3\theta_2) + \text{Be } \dots$	27	$\text{Al } (1 + \cos 2\theta_1 \cos 4\theta_2) + \text{O}_2$ ....	333	
3	$\text{Al } (1 + \cos 3\theta_1 \sin 3\theta_2)$ ....	196	$\text{Al } (\sin 3\theta_1 \sin 4\theta_2)$ $\quad \quad \quad + \text{Be } (0.6) + \text{O}_4 \cos \pi/6$	124	
4	$-\text{Al } (\sin 4\theta_1 \cos 3\theta_2)$ ....	?	$\text{Al } (1 + \cos 4\theta_1 \cos 4\theta_2)$ $\quad \quad \quad + \text{Be } (0.5) - \text{O}_2$	89	
5	$\text{Al } (1 + \cos 5\theta_1 \sin 3\theta_2)$ ....	52	$\text{Al } (\sin 5\theta_1 \sin 4\theta_2)$ $\quad \quad \quad + \text{Be } (0.6) - \text{O}_4 \cos \pi/6$	25	
6	$-\text{Al } (\sin 6\theta_1 \cos 3\theta_2) + \text{Be } \dots$	?	$\text{Al } (1 + \cos 6\theta_1 \cos 4\theta_2) + \text{O}_2$ ....	59	
7	$\text{Al } (1 + \cos 7\theta_1 \sin 3\theta_2)$ ....	13, 3	$\text{Al } (\sin 7\theta_1 \sin 4\theta_2)$ $\quad \quad \quad + \text{Be } (0.5) + \text{O}_4 \cos \pi/6$	11	
8	$-\text{Al } (\sin 8\theta_1 \cos 3\theta_2)$ ....	?	$\text{Al } (1 + \cos 8\theta_1 \cos 4\theta_2)$ $\quad \quad \quad - \text{Be } (0.5) - \text{O}_2$	7	

\* The  $K_2$  peak is resolved.

The contributions to the structure factors of the beryllium atoms are based on two possible arrangements of these atoms. It is assumed that the beryllium atoms are at the centres of groups of four oxygen atoms arranged tetrahedrally, this position being suggested by the arrangement of the Mg atoms in  $\text{MgAl}_2\text{O}_4$ . There are two ways of doing this. The co-ordinates of the typical Be atom are

First arrangement  $\alpha = \pi/4$ ,  $\beta = \pi/6$ ,  $\gamma = \pi/2$ .

Second arrangement,  $\alpha = 3\pi/4$ ,  $\beta = \pi/6$ ,  $\gamma = \pi/2$ .

The first arrangement brings the beryllium ion into much closer proximity to the aluminium ions than the second, and for physical reasons is less probable. If the Be ions are in the second arrangement, the relative position of  $\text{Be}^{++}$  and  $\text{Al}^{+++}$  is almost exactly that of  $\text{Mg}^{++}$  and  $\text{Al}^{+++}$  in  $\text{MgAl}_2\text{O}_4$ . This second arrangement is shown in fig. 1, where it may be compared with that of spinel.

The observations of intensity are not sufficiently refined to distinguish between these two possibilities, or other arrangements of the Be ions. We cannot, therefore, say that our investigation throws any light on the position of the beryllium atom in the structure.

#### 8. *Explanation of Rotating Crystal Photographs.*

In order to show the extent to which the proposed structure explains the photographs obtained with a rotating crystal, we give below a complete analysis of one of the plates. The photograph was taken by rotating the (010) face through  $30^\circ$  about the [100] axis.

Calculation shows that in a rotation of  $30^\circ$ , seventy-five reflexions are possible owing to planes passing through the reflecting position (reflexions  $(h\ k\ l)$  and  $(\bar{h}\ \bar{k}\ \bar{l})$  above and below the main spectrum are treated as identical). Certain of these are eliminated because the reflected ray penetrates into the crystal instead of emerging from the face, and so is absorbed. Such are marked with an asterisk in the table. The structure factor for each reflexion  $(h\ k\ l)$  has been calculated, and its magnitude is indicated in the table by s. (strong) w. (weak) m. (moderate), etc. In estimating these indications of intensity we took as a rough guide the following scale:—

Structure factor involving $\sin \theta_1$ , $\sin 2\theta_1$ , $\sin 3\theta_1$ .....	v.w.
Structure factor about 0.5 Al .....	w.
Structure factor about Al .....	m.
Structure factor $\text{Al}_2$ , or $\text{O}_4$ .....	s.
Structure $\text{Al}_2 + \text{O}_2$ , $\text{Al} + \text{O}_4$ .....	v.s.

Spaces are left blank where the crystal does not pass through the necessary position for reflexion. The table, therefore, gives all the information for constructing a diagram of the reflexions which may be compared with the actual photograph. It tells what reflexions can occur, whether they are cut off by absorption, and whether they should be strong or weak.

Table VI.\*

$l = 0.$											
$k =$	1	2	3	4	5	6	7	8	9	10	11
$h = 0$	—	v.w.	—	m.	—	v.w.	—	w.	—	w.	—
1	m.*	v.w.*	s.	s.	w.	v.w.	s.	m.	v.w.	v.w.	s.
2		v.w.*	v.w.*	v.s.*	v.w.	w.	v.w.	s.	v.w.	m.	v.w.
3						v.w.*	s.				
$l = 1.$											
$k =$	1	2	3	4	5	6	7	8	9	10	11
$h = 0$							v.w.	w.	v.w.	w.	v.w.
1					w.	v.w.	w.	v.w.	v.w.	v.w.	v.w.
2					v.w.	w.	v.w.	m.	v.w.	m.	
3		v.w.	m.	v.w.	m.	v.w.	w.	v.w.			
4					v.w.*	m.*	v.w.*	m.*			
$l = 2.$											
$k =$	1	2	3	4	5	6	7	8	9	10	11
$h = 0$									v.w.	w.	v.w.
1									s.	v.w.	v.w.
2								m.	v.w.	m.	
3							v.w.	v.w.	s.		
4			v.w.	w.	v.w.	v.w.	v.w.	m.			

The photograph is shown as a diagram in fig. 7, the intensity of the spots on it being represented by the thickness of the lines. The diagram calculated from the structure factors is shown beside it for the sake of comparison.

\* In addition to these reflexions (071) is possible with a very small structure factor.

The correspondence is not exact, but is good. We have compared the other photographs with the calculated factors in a similar way, but the results are not given in full, for the sake of brevity; this example will, perhaps, show their nature.

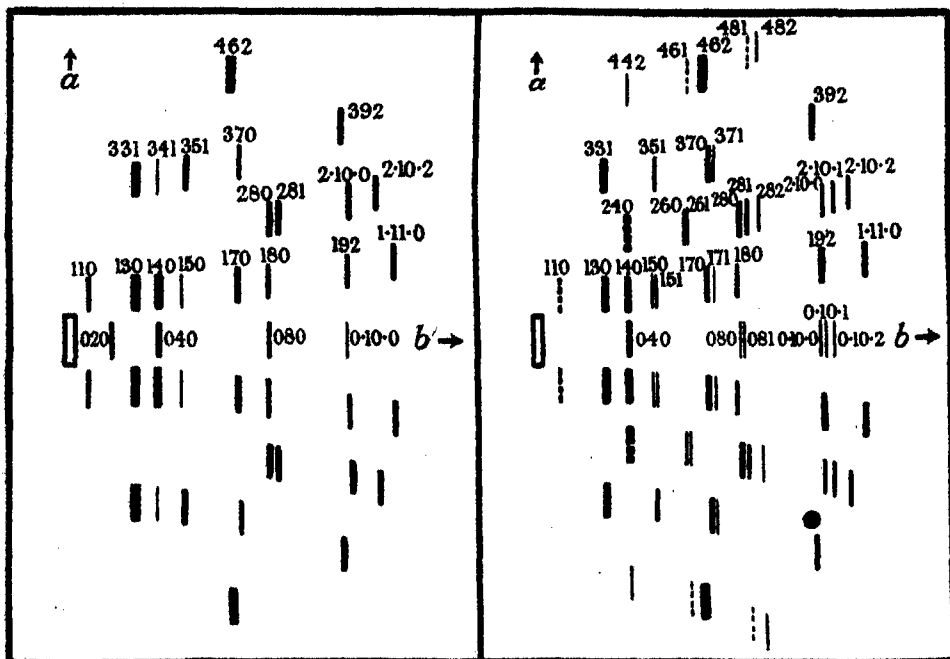


FIG. 7.—Comparison of rotating-crystal photograph (left) with diagram based on calculated structure factors (right). Seventy-five reflexions are possible. Of these forty have a very small structure factor and so have been omitted in the diagram on the right. It will be seen that the remainder are in nearly every case present in the photograph on the left, and that the correspondence of the intensities is satisfactory considering the fact that no allowance has been made for the position of the reflexion. The broken lines represent reflexions that have to pass through the body of the crystal, and so may be expected to be absorbed.

### 9. Calculation of Structure Factors.

The following formulæ have been used in the calculation of the structure factors. If an atom has co-ordinates  $\alpha$ ,  $\beta$ ,  $\gamma$  with reference to a centre of symmetry of the structure, the contribution to the amplitude of the reflected wave, due to this atom and the seven others derived from it by the operation of the symmetry-elements, is given by

$$8A \cos \left\{ (h+k) \frac{\pi}{2} + h\alpha \right\} \cos \left\{ (h+k+l) \frac{\pi}{2} + k\beta \right\} \cos \left\{ l \frac{\pi}{2} + l\gamma \right\},$$

the amplitude contributed by one atom being equal to  $A$ . In the special case when the atoms are on reflexion planes or at symmetry centres the factor 8 becomes a factor 4.

(a) The typical aluminium atom at a symmetry centre has co-ordinates

$$\alpha = \beta = \gamma = 0.$$

The contribution of the four atoms to the structure factor becomes

$$\begin{aligned} 4 A \cos(h+k) \frac{\pi}{2} \cos(h+k+l) \frac{\pi}{2} \cos l \frac{\pi}{2} \\ = 4 A \cos^2(h+k) \frac{\pi}{2} \cos^2 l \frac{\pi}{2}. \end{aligned}$$

The factor is zero unless  $h+k$  and  $l$  are even.

(b) The typical aluminium atom on a reflexion plane has co-ordinates

$$\alpha = 0_1, \quad \beta = \frac{\pi}{2} + 0_2, \quad \gamma = \frac{\pi}{2}.$$

The contribution of the four atoms to the structure factor is

$$\begin{aligned} 4 A \cos \left\{ (h+k) \frac{\pi}{2} + h 0_1 \right\} \cos \left\{ (h+k+l) \frac{\pi}{2} + k \frac{\pi}{2} + k 0_2 \right\} \cos l \pi \\ = 4 A \cos \left\{ (h+k) \frac{\pi}{2} + h 0_1 \right\} \cos \left\{ (h+l) \frac{\pi}{2} + k 0_2 \right\} \cos k \pi \cos l \pi. \end{aligned}$$

(c) We will suppose the oxygen atoms to be exactly in a close-packed assemblage. Then they will not contribute to the structure factor unless  $k, l, \frac{1}{2}(k+l)$  are even. If this condition is satisfied, the contribution of the 16 oxygen atoms is given by

$$\begin{aligned} 16 \cdot O \cdot \cos \left\{ (h+k) \frac{\pi}{2} + h \frac{\pi}{2} \right\} \cos \left\{ (h+k+l) \frac{\pi}{2} + k \frac{\pi}{3} \right\} \cos l \frac{\pi}{2} \\ = 16 \cdot O \cdot \cos h \pi \left( h \frac{\pi}{2} + k \frac{\pi}{3} \right). \end{aligned}$$

The positions of the atoms in the unit cell are summarized below. In each case the position of one atom is given, the rest being derived from it by the operation of the symmetry elements.

Atom.	No. in unit cell.	Linear co-ordinates.	Angular co-ordinates.
Aluminium (sym. centre) ....	4	0, 0, 0	0, 0, 0.
Aluminium (refl. plane) ....	4	0, 0.278b, 0.25c	0, $5\pi/9$ , $\pi/2$ .
Oxygen (refl. plane) ....	4	-0.25a, 0.083b, 0.25c	$-(\pi/2)$ , $\pi/6$ , $\pi/2$ .
Oxygen (refl. plane) ....	4	0.25a, 0.417b, 0.25c	$\pi/2$ , $5\pi/6$ , $\pi/2$ .
Oxygen (general position) ....	8	0.25a, 0.167b, 0	$\pi/2$ , $\pi/3$ , 0.

*Summary.*

The structure of chrysoberyl,  $\text{BeAl}_2\text{O}_4$ , has been examined by the ionization spectrometer and by photographs taken with a revolving crystal. The structure is based on a simple orthorhombic lattice.

$$a = 4.420 \text{ \AA} \quad b = 9.390 \text{ \AA} \quad c = 5.470 \text{ \AA}.$$

The unit cell contains four molecules of  $\text{BeAl}_2\text{O}_4$ . An examination of the observed reflexions shows that the elements of symmetry of the structure are arranged according to the space-group  $V_h^{10}$ .

The positions of the beryllium atoms in the structure cannot be deduced from the results, as these atoms play so little part in X-ray diffraction. The positions of the aluminium and oxygen atoms are determined by nine parameters. Although this large number of parameters makes an exact fixation of every atom difficult, certain interesting features peculiar to the crystal render it possible to obtain a solution of the structure which explains very well the observed data, and which must approximate closely to the actual atomic arrangement.

The ratios and absolute values of the axes given above are in accord with an arrangement of the oxygen atoms in hexagonal close-packing, the distance between nearest atomic centres being  $2.7 \text{ \AA}$ . The relative intensities of the spectra show that this arrangement actually exists. The aluminium atoms lie in spaces between six oxygen atoms. Half of their number are situated at symmetry centres with no degrees of freedom. The others lie on reflexion planes, where their positions are determined by two parameters. An estimate of these parameters can be made by comparing intensities of reflexion. The close-packed arrangement of oxygen ions can be proved to be slightly distorted by the presence of aluminium ions in certain of the spaces referred to above. The amount of the distortion cannot be measured, but so good a quantitative agreement between calculated and observed intensity exists even for planes with large indices, that the distortion cannot be large. The displacement of an oxygen atom from a point determined by close-packing is probably not greater than  $0.2 \text{ \AA}$ .

The structure is in some ways analogous to that of spinel, in spite of the apparent dissimilarity. In chrysoberyl the oxygen ions are in hexagonal close-packing, in spinel they are in cubic close-packing. In both structures the aluminium ions occupy half of the spaces which exist in the structure between six oxygen ions.

Positions may be assigned to the Be ions in  $\text{BeAl}_2\text{O}_4$  which are analogous to those occupied by the Mg ions in  $\text{MgAl}_2\text{O}_4$ . The positions are shown in fig. 1, each divalent metal ion lying between four oxygen ions. The assignment of these positions is purely speculative. The effect on the spectra of the Be ions would be completely masked by a distortion of the close-packed oxygen structure, and our analysis is not sufficiently powerful to detect it.

The analysis is based on a qualitative comparison of reflecting power for various planes, and is therefore far less powerful than the quantitative analysis which can be made with the spectrometer when large crystals are available. On the other hand, about eighty reflexions occur in the photographs and a similar number have been measured with the spectrometer. All these are explained by the structure which is proposed.

The structure is illustrated in figs. 1 and 4, and the positions of the atoms in the unit cell are given in Section 9.

Some of the apparatus used in this investigation has been given to the laboratory by the General Electric Company of America and by Metropolitan Vickers. We have to acknowledge the kind help of Messrs. T. Boyer and J. West, who made many measurements with the spectrometer which we have used in the determination of the structure. We are deeply grateful to Mr. A. Hutchinson, F.R.S., for assisting us to obtain the crystal with which our measurements were made. One of us has been in receipt of a grant from the Department of Scientific and Industrial Research.

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*The Soft X-ray Absorption Limits of Certain Elements.*

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According to Bohr's theory of atomic structure, in the normal configuration of the electrons round the nucleus in any atom, each electron is bound so that its final orbit is that which is in most stable equilibrium with the nucleus and with the other electrons already bound, and the building up of a heavy atom is marked by periods at the end of which an electron group is completed. The orbits of the electrons in the different groups in the atom are characterized by different values of the principal quantum number  $n$ , and within each group the electrons are divided into sub-groups corresponding to different types of orbit characterized by different values of the azimuthal quantum number  $k$ . The more recent developments of Bohr's theory attribute the long periods in the periodic classification of the elements, and certain outstanding features in the physical properties of some of the elements in these periods, to the fact that at certain stages the electrons which are added to the extra-nuclear configuration, as we pass from element to element in the order of increasing atomic number, go to the enlargement of an inner electron group instead of assisting towards the completion of the only partially filled outermost group.

The characteristic X-ray spectra of the elements arise from the creation of a gap in an inner group of electrons and the subsequent readjustment of the atom. The well-known researches of Moseley established the fact that these characteristic X-ray spectra change in an orderly manner, as we pass from element to element down the Periodic Table, the relation between the atomic number and the value of  $\sqrt{(\nu/R)}$  for corresponding X-ray lines of different elements being linear [ $\nu$  denotes the wave-number of the line, and  $R$ , Rydberg's constant].

The existence of the Moseley relation between atomic numbers and the values of  $\sqrt{(\nu/R)}$  for any particular line admits of explanation on Bohr's theory, and is to be attributed to the persistence of the inner electron groups unchanged throughout the elements of atomic numbers higher than those at which each group is completed. A change in the constitution of a group of electrons in the interior of the atom will, however, according to Bohr's theory, reveal itself in the Moseley lines for the absorption limits corresponding to the electronic

sub-groups concerned, by a decrease in the inclination of the lines to the axis of atomic number.

To a first approximation the wave-number corresponding to the energy of ionization of an atom by removal of an electron from an inner electron sub-group is given by the formula  $\nu = R(z - c)^2/n^2$ , where  $c$  is a constant which differs for different electron sub-groups, and  $n$  is the principal quantum number of the group. It may be seen from this equation that the Moseley graph of  $\sqrt{(\nu/R)}$  against atomic number ( $z$ ), for any given sub-group throughout the elements, will be a straight line as long as  $c$  remains constant. The quantity  $c$  depends on the number and arrangement of the electrons in the various groups in the atom, and an increase in the number of electrons in the groups inside the one under consideration, or in that group itself, causes an increase in  $c$ . Hence, at any stage where an electron group is in process of development, the quantity  $(z - c)$ , and therefore the quantity  $\sqrt{(\nu/R)}$  for each of its sub-groups, will increase less rapidly with atomic number than at stages where the group is one of considerable stability.

The theory of the further development of inner electronic groups in the long periods of the periodic classification of the elements may therefore be tested by constructing and investigating the Moseley curves for the  $\sqrt{(\nu/R)}$  values of the electron groups concerned. Unfortunately, practically no measurements are available from X-ray experiments regarding absorption limits of such comparatively low frequencies as those for the special regions of the electronic groups involved. The critical potential method may, however, be applied with advantage, to the determination of the characteristic  $\nu/R$  values in these regions. The method consists in measuring the photoelectric current from a suitably situated metallic plate, caused by the X-radiation emitted by a target of the given element under electronic bombardment, for gradually increased values of the energy of the bombarding electrons. The variation in the energy is produced by a gradually increased potential difference applied to accelerate these electrons. The relation between the photoelectric current and the energy of the electrons is plotted, and critical values of the energy, at which new radiations are produced, are determined from the positions of discontinuities in these curves.

According to the theory, the M electronic group is undergoing its second stage of development between the elements scandium and copper.\* From a consideration of the optical spectra of these elements, Bohr finds in passing

\* Bohr has put forward the view that the group here develops from two sub-groups of four electrons each, to three sub-groups of six electrons each.

from the arc spectrum of potassium ( $z = 19$ ) to the spark spectrum of calcium ( $z = 20$ ), that whereas in the case of potassium the 19th electron is less firmly bound in a  $3_s$  orbit than in either a  $4_1$  or a  $4_2$  orbit, yet in calcium the 19th electron is more firmly bound in a  $3_s$  orbit than in a  $4_2$  orbit, and nearly as firmly bound as in a  $4_1$  orbit. He therefore deduces that in the case of scandium ( $z = 21$ ) the 19th electron will be more firmly bound in a  $3_s$  orbit than in a  $4_1$  orbit, and that at this element the  $3_s$  group of electrons, *i.e.*, the third M subgroup of electrons, begins to develop. From a consideration of the arc spectrum of copper, which in contrast to the complicated spectra of the elements immediately preceding it in the Periodic Table, possesses a comparatively simple structure resembling that of sodium and potassium, Bohr concludes that copper, like these elements, has a symmetrical structure of the inner electron groups, and that a definite stage of development of the M group is complete at copper.

In a paper recently published in the 'Philosophical Magazine,'\* the authors have given an account of a preliminary investigation of critical potentials corresponding to absorption stages for the M electronic groups of iron, nickel, copper, and zinc. The results of these investigations were shown to afford general confirmation of the view that in this region of the periodic classification, the M group of electrons is in process of development. In the present paper an account is given of the results of a more complete investigation of the critical values for the M group for the seven successive elements, chromium, manganese, iron, cobalt, nickel, copper, and zinc ( $z = 24$  to 30 inclusive), undertaken in the hope of obtaining more detailed information with regard to the development of the group.

#### *Apparatus and Method.*

It is essential for the success of the experiments that the electronic bombardment of the element under test should be carried out in a vacuum as nearly perfect as it is possible to obtain. The glass vessel in which the electrodes were contained was therefore constructed without any waxed or cemented joins. It had a tube 2 cm. wide, containing charcoal which was cooled in liquid air during the observations, and it was connected by a side tube S (see fig. 1) through a wide-bore stop-cock and a U-tube immersed in liquid air, with a mercury vapour pump which was maintained in operation throughout the measurements. Before beginning the observations, the apparatus was pumped out and the residual gas removed as completely as possible from the filaments, electrodes, and glass walls, by long-continued heating in an air oven and simultaneous pumping by the mercury vapour pump.

\* Vol. 46, p. 721 (1923).

The metals which formed the targets for the electron bombardment were each 2 cm. long by 1 cm. broad by 0.5 cm. thick, and were grooved down their edges so as to allow them to be held in a row between two parallel thin quartz rods. They were kept apart by pieces of quartz tubing 1.5 cm. long, which fitted over the rods in the spaces between the metals. The ends of the quartz rods fitted into two pieces of soft iron, as shown in the figure (N, N), so that by means of an electro-magnet the whole row could be moved along the horizontal tube U, V, and each target in turn could be placed underneath the tungsten filaments F which supplied the bombarding electron stream. An electrical

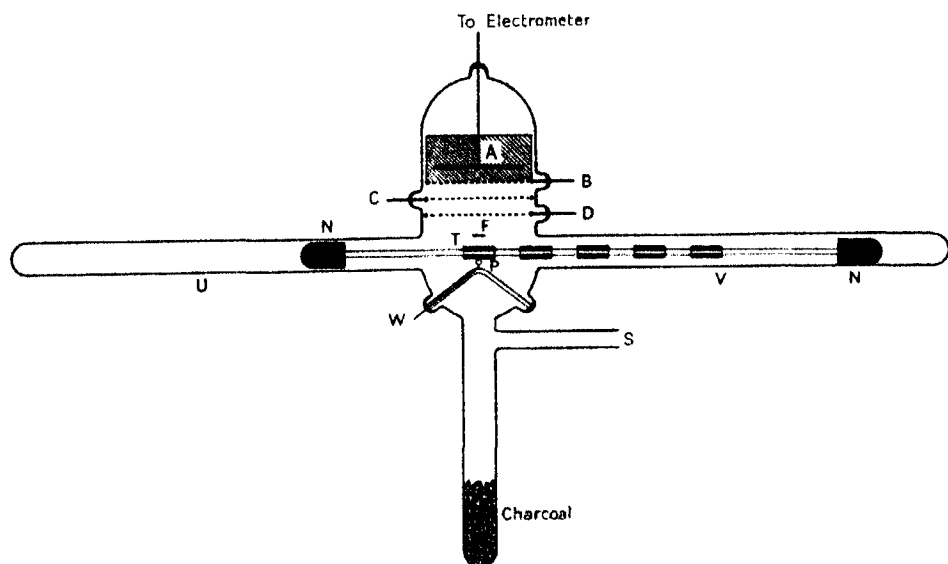


FIG. 1.

connection to the particular element under investigation was made by means of the platinum wire W, at the upper end of which was a small platinum ball P which pressed against the lower face of the target. This arrangement has the great advantage that the element under investigation can be quickly changed so that each element can be examined in turn, and it can be rapidly ascertained whether an indication of a critical point in a current-voltage curve is a genuine effect due to the element, or whether it arises from some other cause, in which case it would be common to the whole series of curves. The row of targets could be turned over in the apparatus by means of the electro-magnet, so that both faces of each target could be used, and the whole row of targets could be moved into one of the side tubes U or V during the preliminary heating of the

apparatus. Thus the surfaces were not contaminated during this process by sputtering from the glowing filaments.

Two V-shaped tungsten filaments, each about 1.5 cm. long in the glowing portion, were contained in the apparatus. These were introduced from opposite sides of the main glass tube and were close together in the same horizontal plane in the position indicated by F in the figure. In some of the earlier observations only one filament was used at a time, the other being kept in reserve; but in nearly all the experiments, the results of which are recorded in the present paper, both filaments were used simultaneously, for it was found that the increased bombardment thus obtained made the effects sought for more marked.

The radiations stimulated by the electron bombardment of the targets were detected by means of their photoelectric effects on a platinum disc A connected to a delicate electrometer. The platinum wire leading to A was protected by earthed guard rings from collecting charges by leakage along the inner or outer surfaces of the glass tube through which it was sealed. A hangs inside a short hollow platinum cylinder B, the base of which is of fine platinum gauze. C and D are two circular pieces of fine platinum gauze, which fill the horizontal section of the central tube of the apparatus, as indicated in the diagram. B, C, and D are about 8 mm. apart, while D is about 13 mm. above the filaments. This arrangement of the plate A and of the three platinum grids is similar to that which has been employed by Horton and Davies in their measurements of the critical potentials for the production of radiation from gases. Fig. 2

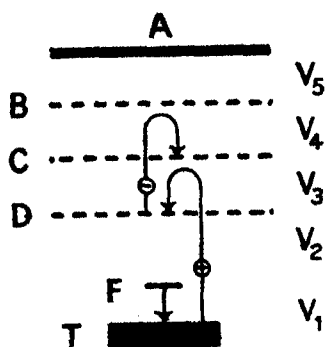


FIG. 2.

is a diagrammatic representation of the arrangement of the electric fields between the various electrodes. This arrangement is the same as that described in our earlier paper, where the reasons for its adoption are given. It secures that the current measured by the electrometer is due only to photoelectric action of radiation on the plate A or the electrode B, this current being positive or negative according as the plate A is negative or positive to the electrode B. The potential difference  $V_1$  could be varied from 0 to 230 volts in steps of one-tenth volt

if necessary, but steps of 1 or 2 volts were generally used. The most suitable values of the other fields employed were found by experiment. For each value of  $V_1$  the photoelectric current was measured for some value of

$V_5$  which was constant in each series of observations, and at the same time the total electron current between the filament and the target was measured by means of a galvanometer. In this way a series of values of the photoelectric current per arbitrary unit bombarding current was obtained, and these values were plotted against the corresponding values of the energy of the bombarding electrons. The latter values were obtained by adding to the applied potential differences  $V_1$  a small correction, which was determined experimentally, by reversing the direction of this potential difference and ascertaining what value of it was just sufficient to reduce the thermionic current measured on the galvanometer to zero, and which thus gave a measure of the initial energy of the emitted electrons. The greatest value of the correction found in any experiment was 1 volt. In many instances series of observations were made in which the photoelectric current for both directions of the field  $V_5$  was measured for every value of  $V_1$ . In this way, data for two curves were obtained simultaneously.

#### *Experimental Results.*

In seeking to locate the critical values of the electron energies for the production of characteristic radiation from any one of the targets, observations were first taken over ranges of values of  $V_1$  of from 40 to 60 volts at a time, and the current-electron energy curves were plotted. The regions at which indications of bends in these curves were found were then investigated in more detail. For each element radiation was first detected when the electron energy was of the order of 10 volts, but it is difficult to be sure that this does not merely correspond to the stage at which the first effect of the general impulse radiation (as distinct from characteristic radiation) becomes measurable with this apparatus.

A statement of results is presented in Table I. The values of the critical potentials given are the means of those deduced from many curves. The positions of the critical points did not, in most cases, vary in the different curves by more than 1 volt from the positions corresponding to the mean values stated.

The voltages and  $\sqrt{(\nu/R)}$  values of the critical points found in the present investigation are given in the second and third columns respectively of the table, and, where measurements by the photoelectric method of critical potentials for these elements, within the same range of voltages, have been published by other investigators, these potentials and their  $\sqrt{(\nu/R)}$  values are given for comparison.

Table I.

Element and Atomic Number.	Critical Values.		Critical Values by other Observers.		Observer.*
	Volts.	$\sqrt{(\nu/R)}$ .	Volts.	$\sqrt{(\nu/R)}$ .	
Cr 24	60	2.10	60.8	2.12	Levi.
	70	2.27			
	143	3.25			
	160	3.44			
	173	3.57			
Mn 25	68	2.24	67	2.22	Levi.
	83	2.47			
	100	2.72			
	152	3.35			
	174	3.58			
Fe 26	184	3.69	46.8 48 50	1.86 1.88 1.92	Rollefson. Thomas. Kurth.
	47	1.86			
	73	2.32			
	90	2.58			
	106	2.80			
Co 27	166	3.50	181.6	3.66	Thomas.
	181	3.66			
	94	2.63			
	113	2.89			
	171	3.55			
Ni 28	191	3.76	79.6 80 100.3 118	2.42 2.43 2.72 2.95	Levi. Foote and Mohler. Levi. Holtmark.
	104	2.77			
	178	3.63			
	196	3.80			
Cu 29	112	2.88	106	2.80	Kurth.
	193	3.77			
	206	3.90			
Zn 30	119	2.96			
	200	3.84			
	214	3.98			

\* Miss Levi, see<sup>1</sup> McLennan, 'Nature,' vol. 113, p. 217 (1924), G. R. Rollefson, 'Physical Review,' vol. 23, p. 35 (1924). This author also finds critical potentials for iron at 81.7, 95.4, 111.2, 130.4, 140.9, 153.7, 160.1 and 171.1 volts. C. H. Thomas, 'Physical Review,' vol. 25, p. 322 (1925). This author finds critical potentials for iron, as well as those given in the table, at 51.3, 54.6, 62, 75.3, 82.7, 94.8, 103.5, 112.2, 131.8, 158.5, 169.4, 192 and 221.3 volts. E. H. Kurth, 'Physical Review,' vol. 18, p. 461 (1921), F. L. Mohler and P. D. Foote, 'Bureau of Standards, Sci. Paper,' No. 425 (1922). J. Holtmark, 'Physikal. Zeits.,' vol. 24, p. 225 (1923).

Typical curves illustrating the several critical potentials found for each of the elements, chromium, manganese, iron, cobalt, nickel, copper, and zinc are given in figs. 3, 4, 5, 6, 7, 8, and 9 respectively.

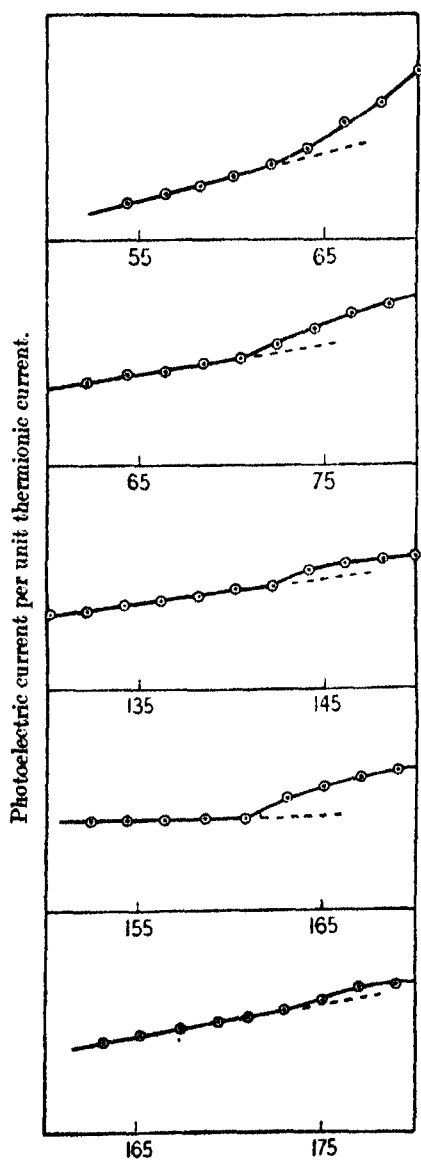


FIG. 3.—Chromium.

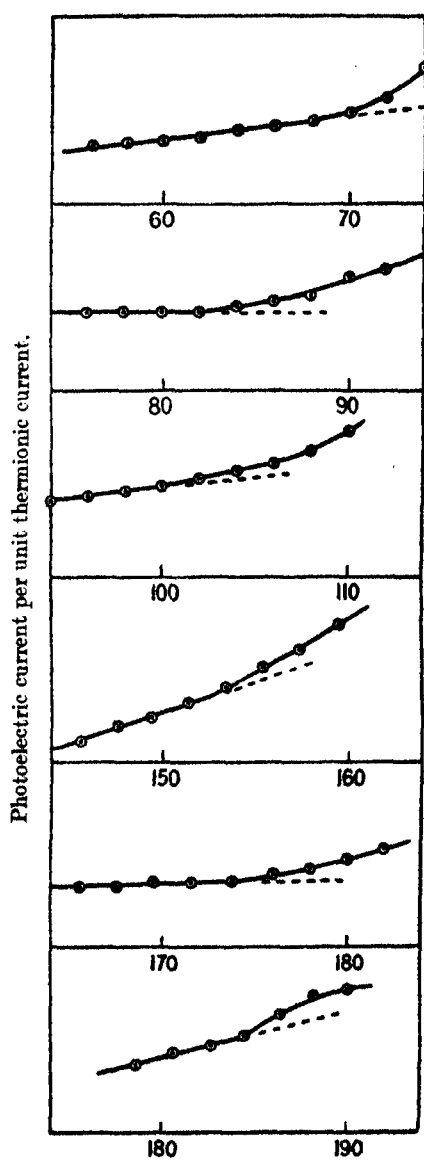


FIG. 4.—Manganese.



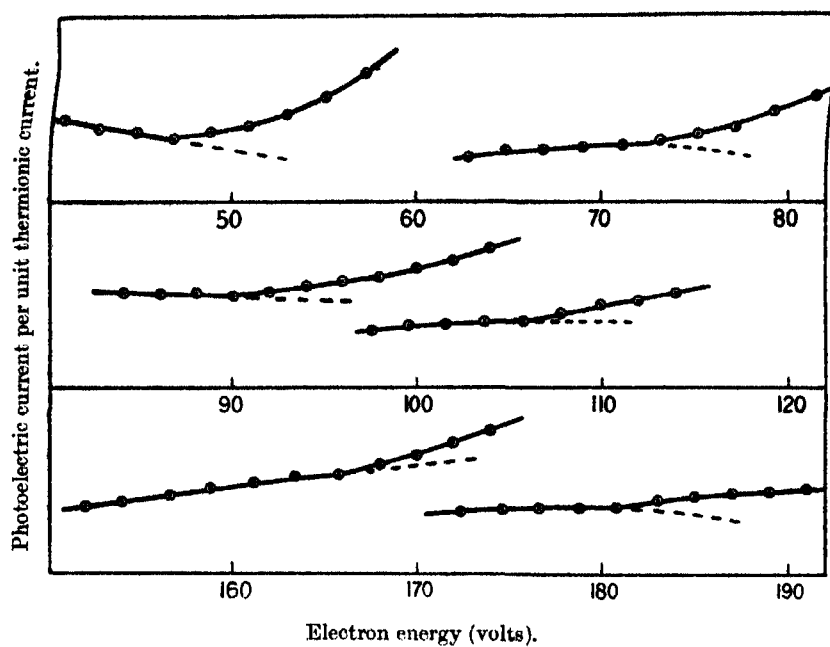


FIG. 5.—Iron.

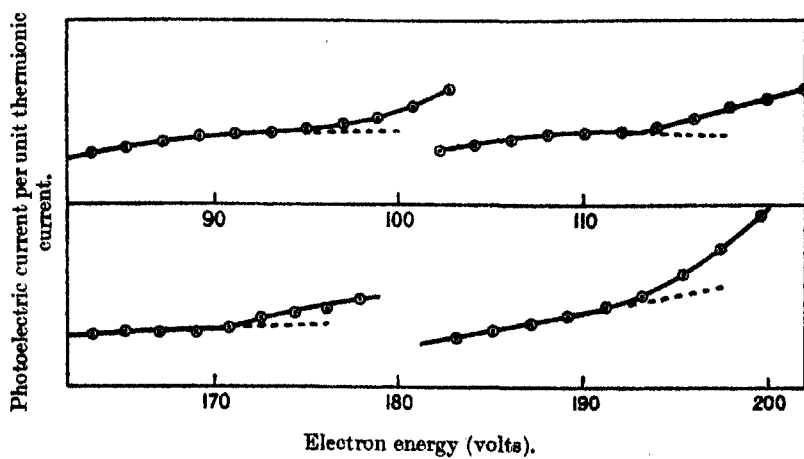


FIG. 6.—Cobalt.

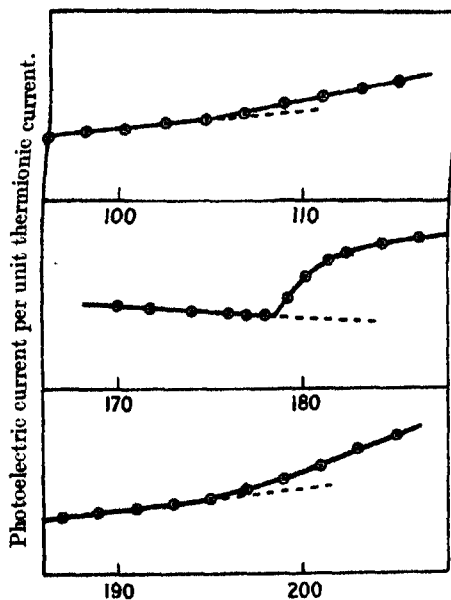


FIG. 7.—Nickel.

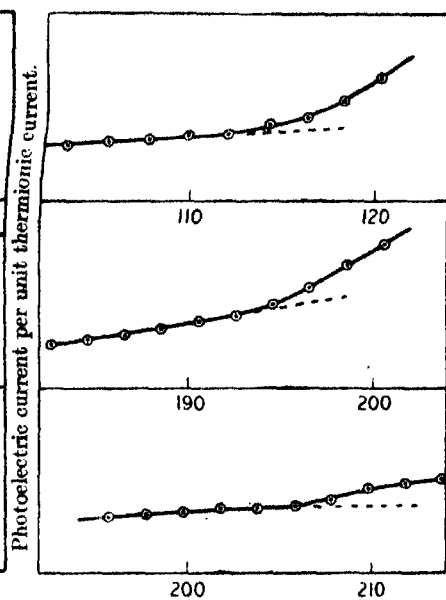


FIG. 8.—Copper.

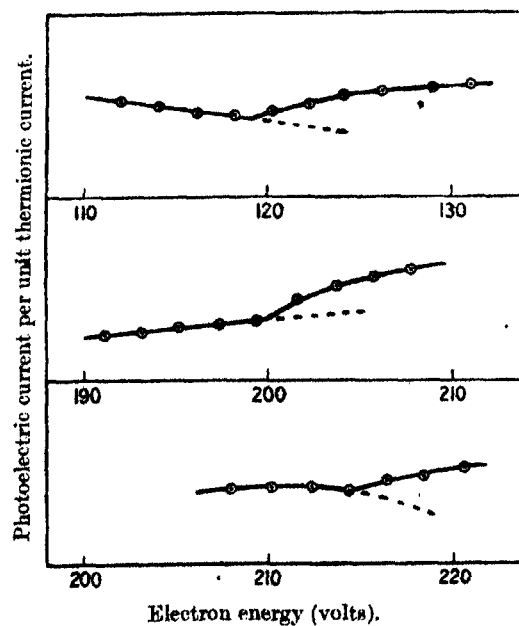


FIG. 9.—Zinc.

*Discussion and Interpretation of Results.*

Coster\* has shown that nearly all the lines of the X-ray spectra of the heavier elements can be arranged in a simple scheme involving the existence of one K level, three L levels, five M levels, and seven N levels, and sometimes O and P levels. Five M absorption edges have been measured spectroscopically for uranium and thorium and three for bismuth. The levels are denoted by the symbols  $M_I$ ,  $M_{II}$ ,  $M_{III}$ ,  $M_{IV}$ ,  $M_V$ ;  $M_I$  having the highest frequency. For elements of lower atomic number the difference between the levels  $M_{II}$  and  $M_{III}$ , and the difference between the levels  $M_{IV}$  and  $M_V$ , becomes inappreciable, and the Moseley lines for these pairs of levels are identical in the region of the Periodic Table under consideration. It will be shown that the critical potentials which have been measured in the present investigation correspond to the removal of electrons from the groups associated with the  $M_I$  and  $M_{II, III}$  levels.

Recent investigations of X-ray absorption spectra by photographic methods have shown that these spectra do not consist simply of regions of continuous absorption, bounded on their long wave-length side by a single sharp edge, as was at first thought; but that these long wave-length boundaries have a definite "fine structure." The photographs show distinct white lines, sometimes three in number, separated from each other by dark bands, the most intense of the lines lying on the long wave-length side and coinciding in position with the previously measured absorption edge hitherto taken as giving the frequency of the level concerned. Nishina,† for instance, in the case of the  $L_{III}$  level has measured two absorption lines for several elements and three for holmium, and his measurements of the principal (or long wave-length) line agree within the limits of experimental error with the values of  $L_{III}$  tabulated by Bohr and Coster‡ for these elements, from previous measurements and computations.

Before the fine structure of an absorption limit had been observed experimentally, Kossel§ had predicted that such a structure should exist, and had suggested that a definite selective line absorption should be found on the long wave-length side of a continuous absorption stage, corresponding to displace-

\* D. Coster, 'Zeit. f. Phys.,' vol. 5, p. 139 (1921), and vol. 6, p. 185 (1921).

† Y. Nishina, 'Phil. Mag.,' vol. 49, p. 521 (1925).

‡ N. Bohr and D. Coster, 'Zeit. f. Phys.,' vol. 12, p. 342 (1922).

§ W. Kossel, 'Verh. Deutsch. Phys. Gesell.,' vol. 18, p. 339 (1916).

ments of an electron from an X-ray level to the various virtual orbits beyond the periphery, or boundary of the atom in its normal state. It seems probable that the structure observed in the more recent work is to be accounted for by the line absorption which Kossel predicted, and as will be shown in the following pages, it seems reasonable to associate the several critical potentials measured for each element examined in the course of this investigation, with electron displacements of this kind from the orbits connected with the  $M_I$  and  $M_{II, III}$  levels.

The recent results suggest that the values given for absorption limits from early observations correspond not to the ionization of the atom by the complete detachment from it of an electron from the K, L, or M, etc., groups, but to the displacement of one of these electrons to the normal boundary of the atom, *i.e.*, to the region of the most loosely attached electrons in the normal state of the atom. This region we shall call the periphery to distinguish it from the exterior virtual orbit region which is normally unoccupied. There are, therefore, four regions to be considered in connection with the extra-nuclear electrons of atoms, namely, (a) the region of the completely filled electron groups; (b) the periphery, *i.e.*, the region of the most loosely attached electrons in the normal atom; (c) the region of the virtual orbits, which is beyond the periphery; and (d) the "infinite distance" region, the transportation of an electron to which leaves the atom in an ionized state. As we pass from heavy to light elements, the region of virtual orbit levels becomes more and more important in comparison with the levels of the inner region of the atom.

Comparisons of measured X-ray emission lines and the associated absorption limits show that the latter correspond to the transportation of electrons from the various inner electron groups to the periphery. Fig. 10 and Table II are given for reference. The former is a diagrammatic scheme of the energy levels in the atom, and shows the transitions which give rise to the various X-ray emission lines. Bohr's notation for the levels is used, and for the emission lines Siegbahn's notation as revised by Coster. Table II gives Bohr's scheme of the electron groupings in the various atoms and the number of electrons describing orbits of the various  $n_k$  types, where  $n$  is the principal quantum number of the orbit and  $k$  the azimuthal quantum number. The orbits of the type  $n_k$  are further differentiated by the introduction of a third quantum number  $j$ , which is equal to the azimuthal quantum number  $k$ , or to  $(k - 1)$ , but which never has the value zero. It is because of this further differentiation that there are more L, M, and N levels shown in fig. 10 than there are L, M, and N,  $n_k$  groups in Table II.

Table II.

	K.	L.	M.	N.	O.	P.	Q.
$\begin{array}{c} n_k. \\ z \end{array}$	1 <sub>1</sub>	2 <sub>1</sub> 2 <sub>2</sub>	3 <sub>1</sub> 3 <sub>2</sub> 3 <sub>3</sub>	4 <sub>1</sub> 4 <sub>2</sub> 4 <sub>3</sub> 4 <sub>4</sub>	5 <sub>1</sub> 5 <sub>2</sub> 5 <sub>3</sub> 5 <sub>4</sub> 5 <sub>5</sub>	6 <sub>1</sub> 6 <sub>2</sub> 6 <sub>3</sub> 6 <sub>4</sub> 6 <sub>5</sub> 6 <sub>6</sub>	7 <sub>1</sub> 7 <sub>2</sub>
1 H	1						
2 He	2						
3 Li	2	1					
4 Be	2	2					
5 B	2	2 (1)					
10 Ne	2	4 4					
11 Na	2	4 4	1				
12 Mg	2	4 4	2				
13 Al	2	4 4	2 1				
18 A	2	4 4	4 4				
19 K	2	4 4	4 4	1			
20 Ca	2	4 4	4 4	2			
21 Sc	2	4 4	4 4 1	(2)			
22 Ti	2	4 4	4 4 2	(2)			
29 Cu	2	4 4	6 6 6	1			
30 Zn	2	4 4	6 6 6	2			
31 Ga	2	4 4	6 6 6	2 1			
36 Kr	2	4 4	6 6 6	4 4			
37 Rb	2	4 4	6 6 6	4 4	1		
38 Sr	2	4 4	6 6 6	4 4	2		
39 Y	2	4 4	6 6 6	4 4 1	(2)		
40 Zr	2	4 4	6 6 6	4 4 2	(2)		
47 Ag	2	4 4	6 6 6	6 6 6	1		
48 Cd	2	4 4	6 6 6	6 6 6	2		
49 In	2	4 4	6 6 6	6 6 6	2 1		
54 X	2	4 4	6 6 6	6 6 6	4 4		
55 Cs	2	4 4	6 6 6	6 6 6	4 4	1	
56 Ba	2	4 4	6 6 6	6 6 6	4 4	2	
57 La	2	4 4	6 6 6	6 6 6	4 4 1	(2)	
58 Ce	2	4 4	6 6 6	6 6 6 1	4 4 1	(2)	
59 Pr	2	4 4	6 6 6	6 6 6 2	4 4 1	(2)	
71 Lu	2	4 4	6 6 6	8 8 8 8	4 4 1	(2)	
72 Hf	2	4 4	6 6 6	8 8 8 8	4 4 2	(2)	
79 Au	2	4 4	6 6 6	8 8 8 8	6 6 6	1	
80 Hg	2	4 4	6 6 6	8 8 8 8	6 6 6	2	
81 Tl	2	4 4	6 6 6	8 8 8 8	6 6 6	2 1	
86 Nt	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4	
87 —	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4	1
88 Ra	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4	2
89 Ac	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4 1	(2)
90 Th	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4 2	(2)
116 ?	2	4 4	6 6 6	8 8 8 8	8 8 8 8	6 6 6	4 4

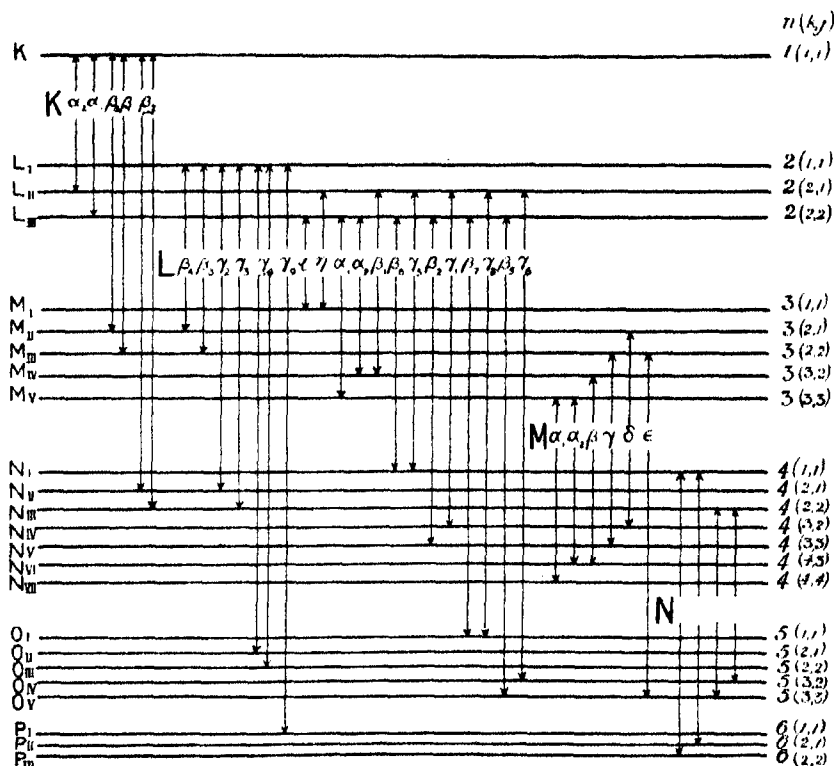


FIG. 10.

In Table III the  $\nu/R$  values of certain absorption limits are compared with the  $\nu/R$  values of selected X-ray emission lines.\* Each line is designated in the table by the difference of the two levels between which the electron transition resulting in the emission of the line occurs. In view of the suggestion that the measured absorption limits do not correspond to the true energies of the levels, the symbols for levels deduced from measured absorption limits are given in square brackets [ ]. Where a difference of two levels is concerned, the brackets are omitted because the distinction is unnecessary. It may be seen that for the lighter elements for which the comparison of any particular pair of  $\nu/R$  values is made, the agreement is very much better than for the heavier elements to which the same comparison is extended. For instance, in the case of the elements from  $z = 40$  to  $z = 55$ , for which the values  $[L_{III}]$  and  $L_{III} - N_V$  are given, the difference of these values for the lighter elements is about 0.6 or less, while for the heavier elements it increases to several times this amount and cannot

\* These values are taken from 'Spektroskopie der Röntgenstrahlen,' Siegbahn.

Table III.

Ele- ment.	Absorp- tion Limit.	$\nu/R$ .	Line.	$\nu/R$ .	Absorp- tion Limit.	$\nu/R$ .	Line.	$\nu/R$ .	Remarks.
Al 13	[K]	114.67	K—M <sub>II, III</sub>	114.76					
Ti 22	"	365.43	K—N <sub>II, III</sub>	365.42					
V 23	"	402.27	"	402.42					
Cr 24	"	441.14	"	440.86					
Mn 25	"	482.36	"	481.34					
Fe 26	"	524.34	"	523.54					
Co 27	"	568.90	"	567.63					
Ni 28	"	612.00	"	613.48					
Cu 29	"	661.06	"	661.30					
Zn 30	"	702.98	"	711.31					
Ge 32	"	817.57	"	819.58					
Se 34	"	930.82	"	932.28					
Rb 37	"	1119.1	"	1118.6					
Sr 38	"	1184.1	"	1185.4					
Zr 40	"	1326.1	"	1324.4	[L <sub>III</sub> ]	163.5	L <sub>III</sub> —N <sub>V</sub>	163.5	
Nb 41					"	174.4	"	174.4	
Mo 42					"	186.2	"	185.62	
Rh 45					"	220.9	"	221.07	
Ag 47					"	247.3	"	246.7	Transition to N <sub>V</sub> no longer possi- ble.
Sb 51					"	305.3	"	302.09	
Te 52					"	320.1	"	316.84	
I 53					"	336.0	"	331.87	
Cs 55					"	369.3	"	363.58	
Hg 80	[M <sub>V</sub> ]	99.8	M <sub>V</sub> —N <sub>VII</sub>	99.58					
Er 68	"	104.0	"	103.7					
Yb 70	"	112.8	"	112.2					
Lu 71	"	117.2	"	116.5					Transition to N <sub>VII</sub> no longer possible.
Ta 73	"	127.8	"	125.9	[L <sub>III</sub> ]	752.1	L <sub>III</sub> —O <sub>V</sub>	751.56	
W 74					"	852.0	"	851.57	
Pt 78					"	878.5	"	877.70	Transition to O <sub>V</sub> no longer possi- ble.
Au 79									
Tl 81					"	933.2	"	931.4	
Pb 82					"	960.5	"	959.72	
Bi 83					"	990.0	"	987.98	
Th 90	[M <sub>V</sub> ]	244.90	M <sub>V</sub> —P <sub>III</sub>	242.8	"	1200.6	"	1194.94	
U 92	"	261.03	"	259.3	"	1264.3	"	1258.43	

be considered as within the limits of experimental error. The initial level N<sub>V</sub> concerned in the emission of the line L<sub>III</sub> — N<sub>V</sub> is associated with orbits of the type 4<sub>s</sub>, and a consideration of the region of Table II dealing with elements from  $z = 40$  to  $z = 55$  shows that up to  $z = 47$  the 4<sub>s</sub> sub-group is in process of development, and that N<sub>V</sub> may therefore be regarded as a peripheral level. For the elements between  $z = 47$  and  $z = 55$ , the electrons in this sub-group, which at silver ( $z = 47$ ) has attained a considerable degree of stability, become

more and more firmly bound to the nucleus on account of its increasing positive charge, and can no longer be considered as comparable with the electrons in the outer sub-groups as regards firmness of binding. For these elements, therefore, the level  $N_V$  differs considerably from a peripheral level.  $[L_{III}]$  for these elements must of necessity be larger than  $L_{III} - N_V$ , because transitions to the level  $N_V$  are out of the question on account of the completeness of the  $4s$  group in this region. The fact that the discrepancy between  $[L_{III}]$  and  $L_{III} - N_V$  occurs just at the stage where  $N_V$  can no longer be reasonably considered as a peripheral level supports the view that  $[L_{III}]$  is not a true measure of  $L_{III}$ , but gives simply the energy difference between  $L_{III}$  and the periphery. The evidence contained in Table III leads to similar conclusions regarding the other measured absorption limits employed, and supports the view that most of the absorption limits, which have been measured, should be attributed to the removal of an inner electron to a peripheral orbit and not to the "infinite distance" region, and that other selective absorption stages corresponding to transitions to the virtual orbit region might be expected on the short wave-length side of these.

An objection to the suggestion that all the accepted values of absorption limits should be explained in this way might be raised on the ground that the validity of the frequency relations connecting levels and emission lines, when absorption limits and emission lines are employed, then seems to involve the assumption that an electron from an inner group can be removed, irrespective of its original orbit, to the same final sub-group, an assumption which would include the occurrence of several transitions forbidden by the selection principle. For instance,  $L_{\alpha_1} = L_{III} - M_V$ . The fact that the difference between  $[L_{III}]$  and  $[M_V]$  is equal to  $L_{\alpha_1}$  presents no theoretical difficulty if  $[L_{III}] = L_{III}$ , and  $[M_V] = M_V$ . If, however, we consider an atom in which an electron is removed at the absorption stage from  $L_{III}$  to  $O_V$ , then in order that the above relation may be strictly true,  $[M_V]$  must correspond to a transition from  $M_V$  to  $O_V$ . Since the azimuthal quantum number characterizing the electron orbits of the  $O_V$  level is the same as that characterizing orbits of the  $M_V$  level, this transition is forbidden by the selection principle for the azimuthal quantum number, according to which, only those transitions for which  $\Delta k = \pm 1$  can occur.\* The frequency relations, as applied to the generally accepted values of the absorption limits, are, however, probably not strictly accurate relations, but merely approximations, which are accurate within the limit of experi-

\* The allocation of  $k$  and  $j$  values to the various levels in fig. 10 and the selection principle here quoted are in accordance with the scheme put forward by Landé, 'Zeit. f. Phys.,' vol. 16, p. 391 (1923).



mental error, owing to the existence of peripheral orbits of more than one  $n_k$ , whose difference in energy value is negligible in comparison with the energy values of the inner electron groups. To illustrate this, we may continue the consideration of the case quoted above, namely, the forbidden transition  $O_V$  to  $M_V$ . Referring to Table III, we find that the comparison between  $[L_{III}]$  and  $L_{III} - O_V$  is not extended to atomic numbers below 74. With regard to the transition  $O_V$  to  $L_{III}$ , i.e., the line  $L_{\beta_3}$ , Coster\* found that it could not be measured for elements of atomic number lower than 73, and that for several of the rare earths and for barium ( $z = 56$ ) and caesium ( $z = 55$ ) the white absorption line  $[L_{III}]$  was found on the photographic plate in the position where  $L_{\beta_3}$  was to be expected. We are thus justified in concluding that from atomic number 73 to atomic number 55,  $[L_{III}]$  is practically identical with  $L_{III} - O_V$ . The table shows that in this region  $[M_V]$  is very nearly the same as  $M_V - N_{VII}$ . If the relation  $L_{III} - M_V = L_{\alpha_1}$  is valid in this region when the values  $[L_{III}]$  and  $[M_V]$  are employed, it suggests that  $N_{VII} - O_V$  for these elements is negligible in comparison with  $M_V$  and  $L_{III}$ . Inspection of Table II shows that in the region of the elements considered, the development of the third O sub-group—to which  $O_V$  belongs—is arrested while the development of the fourth N sub-group—to which  $N_{VII}$  belongs—occurs, so that the suggestion that  $N_{VII} - O_V$  is small is in accord with Bohr's scheme.

In applying critical potential methods to the investigation of the X-ray region of various atoms, it must be borne in mind that the critical potentials are indicated by an increased rate of production of photoelectrons, i.e., by an increase in the amount of X-radiation emitted. Nevertheless the critical potentials so obtained will not be connected by the quantum relation with the frequencies of emission lines, but with the frequencies of selective absorption stages, for emission of radiation cannot occur until gaps have been created in inner electron groups by the transference of energy to the atoms, resulting in the transportation of electrons from the inner part of the atom either to the periphery, or to the virtual orbit region, or to the infinite distance region. With regard to transitions to virtual orbits, the more remote the virtual orbit from the inner part of the atom, the greater the number of quanta of radiation likely to be emitted in the process of reorganization of the atom. Hence we may expect to obtain indications of critical potentials corresponding to transitions of an electron from one particular inner group to more and more remote virtual orbits, until a stage is reached when the additional radiations, made possible by the more remote transferences, are no longer of such wave-length

\* D. Coster, 'Phil. Mag.,' vol. 44, p. 546 (1922).

as to be photoelectrically active. We may therefore expect to be able to identify several of the critical potentials found for any one element with displacements from the same inner electron group.

To assist in the interpretation of the critical potentials measured in this investigation, the Moseley lines for the values  $[M_I]$ ,  $[M_{II}]$ ,  $[M_{III}]$ ,  $[M_{IV}]$  and  $[M_V]$  have been plotted for atomic numbers below 60, *i.e.*, the values of  $\sqrt{\nu/R}$  for these absorption limits have been plotted as ordinates and the atomic numbers as abscissæ. The values for the M absorption limits in this region of atomic number have not been measured directly, but have been computed from the frequency relations given below in cases where the limits and lines required for the computation have been measured directly:—

$$\begin{aligned} [M_I] &= [L_{III}] - L_i = [L_{II}] - L_n, \\ [M_{II}] &= [K] - K_{\beta_n} = [L_I] - L_{\beta_n}, \\ [M_{III}] &= [K] - K_{\beta_1} = [L_I] - L_{\beta_1}, \\ [M_{IV}] &= [L_{III}] - L_{a_2} = [L_{II}] - L_{\beta_1}, \\ [M_V] &= [L_{III}] - L_{a_1}. \end{aligned}$$

L critical absorption wave-lengths have been measured spectroscopically for 23 elements between uranium ( $z = 92$ ) and silver ( $z = 47$ ), and the necessary emission lines have been measured for most of these elements. By using the frequency relations

$$\begin{aligned} [L_{II}] &= [K] - K_{a_2}, \\ [L_{III}] &= [K] - K_{a_1}, \end{aligned}$$

it is possible to compute the values of L critical absorption frequencies from observation of K absorption limits and K emission lines, and by using the values of the L absorption limits thus computed, to calculate the values of  $[M_I]$ ,  $[M_{IV}]$  and  $[M_V]$ , from the relations already given, even in cases where the L critical absorption wave-lengths have not been measured directly. The square roots of the quantities  $\nu/R$  have been worked out down to  $z = 40$  by Bohr and Coster,\* and by Nishina,\* and are plotted against the corresponding atomic numbers in fig. 11. The values of  $[M_{II, III}]$  for elements of lower atomic number than 40 can be calculated, but these points have not been marked in the figure on account of their being very irregularly situated. The accuracy of these computed values for elements of low atomic number seems doubtful, for if the values obtained for the K absorption limit by different

\* *Loc. cit.*

observers are employed, very different values of the M absorption limits result from the computation.\*

The  $\sqrt{\nu/R}$  values for the critical potentials measured in this investigation are also plotted in fig. 11 against the appropriate atomic numbers, and are marked  $\backslash$ . It will be seen that a series of straight lines *a, b, c*, etc., which are roughly parallel to each other can be drawn connecting points for the different elements investigated, thus suggesting that the points on any one line correspond

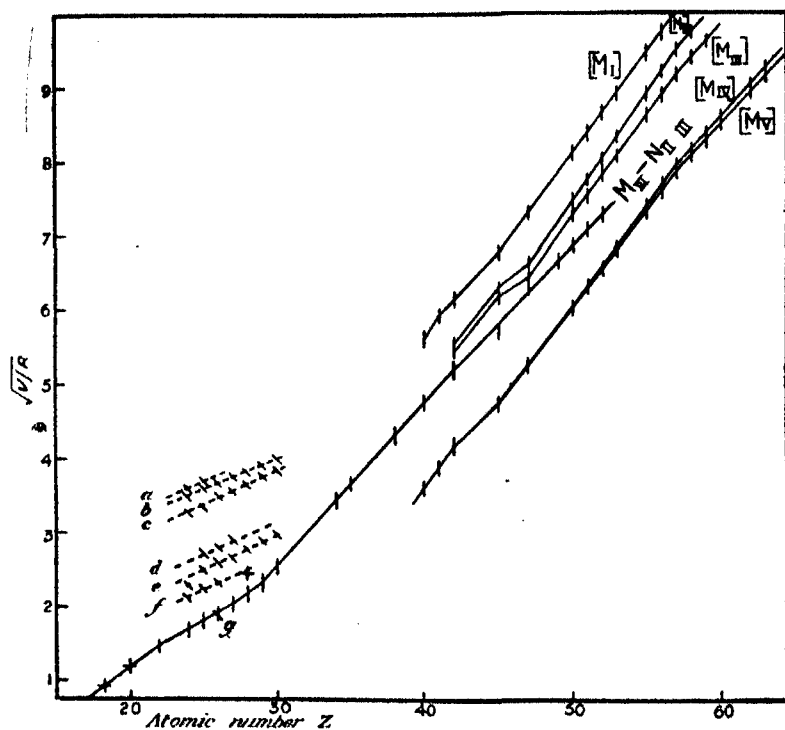


FIG. 11.— $\backslash$ , present research ; +, other observers ; |, computed values.

to similar transitions. It may be noticed that the value for nickel ( $z = 28$ ) corresponding to the critical potential at about 80 volts (marked +) measured by Foote and Mohler, and by Miss Levi, lies near to one of these lines.

\* By means of a relation connecting the difference between [K] and  $K_{\beta}$  with atomic number, which he has deduced from measurements on the four elements Ni, Rh, Mo and W, Walter has calculated values of the K absorption limit for elements of low atomic number from measurements of  $K_{\beta}$ , and hence has computed values of [M<sub>III</sub>] (B. Walter, 'Zeit. f. Phys.', vol. 30, p. 357 (1924)). These values show a more regular variation with atomic number than the values computed by Bohr and Coster, but Walter's procedure has been criticized by Coster (D. Coster, 'Zeit. f. Phys.', vol. 31, p. 898 (1925)). Walter's values are not included in fig. 11.

The comparison of the  $\nu/R$  values of  $[K]$  and  $K - N_{II, III}$ , for the elements of atomic numbers between 22 and 29, in Table III suggests that at the K absorption limit, an electron is transported from the K level to the  $N_{II, III}$  level, which according to Bohr's scheme is a peripheral level for these elements. We have, therefore, plotted in fig. 11 the Moseley line for the quantity  $M_{III} - N_{II, III}$  which can be obtained from the difference of two K emission lines,  $K_{\beta_2}$  and  $K_{\beta_1}$ . These lines have been measured for the elements from titanium ( $z = 22$ ) to tellurium ( $z = 52$ ). The Moseley line thus obtained is prolonged to pass through a point for calcium ( $z = 20$ ) corresponding to a wave-length measured by Millikan and Bowen,\* and shown by them to be connected with an electron transition from  $N_I$  to  $M_{II, III}$ . The Moseley line for  $M_{III} - N_{II, III}$  also passes through the point corresponding to the first radiation potential of argon ( $z = 18$ ), found by Horton and Davies,† which is associated with a transition from  $M_{II, III}$  to an N level. It passes almost through the point,  $g$ , corresponding to the lowest critical potential for iron, measured in this research, but it does not pass through any of the points measured for the other elements. It will be seen from fig. 11 that all the points for these elements lie definitely above the  $M_{III} - N_{II, III}$  line. It thus seems clear that the lowest critical potential for iron is to be associated with the transition  $M_{II, III} - N_{II, III}$ , whereas the lowest values for the other elements must correspond either to the removal of an electron from the  $M_{II, III}$  level‡ to orbits further out than those associated with the  $N_{II, III}$  level, or to the removal of an electron from a different initial level, *e.g.*,  $M_I$ .

It is interesting to note that the  $[M_{II}]$  and  $[M_{III}]$  Moseley lines in fig. 11 if prolonged to lower atomic numbers, must merge into the  $M_{III} - N_{II, III}$  line before the region of the elements under consideration. On the view that the accepted values of the  $[M_{II, III}]$  limits correspond to transitions from  $M_{II, III}$  not to infinity but to the periphery of the atom, this merging together of these lines in this region is readily interpreted in conjunction with Table II; for whereas for elements of atomic number greater than that of Kr ( $z = 36$ ), the level  $N_{II, III}$  could not be included in the periphery, on account of the electron groups  $4_1$  and  $4_2$  containing their full complement of electrons for the first stage of development, yet for the elements of atomic number between 24 and 30, this level might well be termed a peripheral level, and the accepted values of  $[M_{II, III}]$  might well be identical with the values of  $M_{II, III} - N_{II, III}$ .

\* R. A. Millikan and I. S. Bowen, 'Physical Review,' vol. 23, p. 1 (1924).

† F. Horton and A. C. Davies, 'Roy. Soc. Proc.,' A, vol. 97, p. 1 (1920).

‡ The difference between the levels  $M_{III}$  and  $M_{II}$  is negligible in this region.

The electron transition  $M_{II,III}$  to  $N_{II,III}$  would appear to constitute an instance of violation of the selection principle governing change of the azimuthal quantum number. However, the amount of energy involved in transferring an electron from the  $M_{II,III}$  level to a peripheral level to which it may go in accordance with the selection principle, is not likely to differ by an appreciable amount from the energy corresponding to  $M_{II,III}-N_{II,III}$  for the elements we have investigated. This is shown by Table IV, in which the values of  $v/R$  for  $M_{II,III}-N_I$ ,  $M_{II,III}-N_{II,III}$ , and  $M_{II,III}-N_{IV,V}$  have been computed for elements between atomic numbers 40 and 50, and are set out for comparison. It may be seen from the table that the differences in the values of these quantities for any one element decrease with atomic

Table IV.

Element.	$K_{\alpha_2} + L_{\gamma_1} - K_{\beta_1}$ ( $M_{II,III} - N_I$ ).	$K_{\beta_2} - K_{\beta_1}$ ( $M_{II,III} - N_{II,III}$ )	$K_{\alpha_2} + L_{\gamma_1} - K_{\beta_1}$ ( $M_{II,III} - N_{IV,V}$ ).
Zr 40.....	20.55	22.7	23.9
Nb 41.....	—	24.4	25.88
Mo 42.....	24.50	26.8	28.83
Rh 45.....	31.23	32.3	36.94
Pd 46.....	33.08	36.1	39.20
Ag 47.....	34.62	39.5	41.26
Cd 48.....	37.20	42.0	44.42
In 49.....	40.10	43.6	47.81
Sn 50.....	42.62	47.0	50.77

number, and it can be shown by plotting Moseley curves for the values that the lines are indistinguishable, on the scale of fig. 11, for atomic numbers below 30. There seems little doubt, therefore, that the portion of the  $M_{II,III}-N_{II,III}$  Moseley line in fig. 11 for atomic numbers below 30 represents the values of  $[M_{II,III}]$  which are analogous to the values plotted for higher atomic numbers.

The Moseley line for the  $[M_I]$  values is plotted separately in fig. 12, and for comparison with this the line for values of  $L_{\gamma_1} - L_{\gamma_2}$ , which gives the difference  $M_I - N_I$ , have been calculated and plotted. It is clear from the figure that these lines, if extended, must merge together before the region of atomic numbers we are considering, and by analogy with the course of the  $M_{III}-N_{II,III}$  line in fig. 11 it seems probable that the  $[M_I]$  and  $M_I - N_I$  lines continue as the line *d* in our figures.

The foregoing considerations, therefore, suggest that the points on the lines marked *e*, *f*, and *g* are to be connected with transitions of an electron

from the  $M_{II, III}$  level, the point on the line  $g$  corresponding to a displacement to the periphery, while the points on the lines marked  $a$ ,  $b$ ,  $c$ , and  $d$  are to be associated with transitions of an electron from the  $M_I$  level, the points on the line  $d$  corresponding to transitions to the periphery. The decrease in the inclination of the  $M_{II, III} - N_{II, III}$  line to the axis of atomic number in passing through the elements under consideration, and the slope of the parallel lines on which the observed points can be fitted, support Bohr's view that a development of the M group is in progress in this region of atomic number.

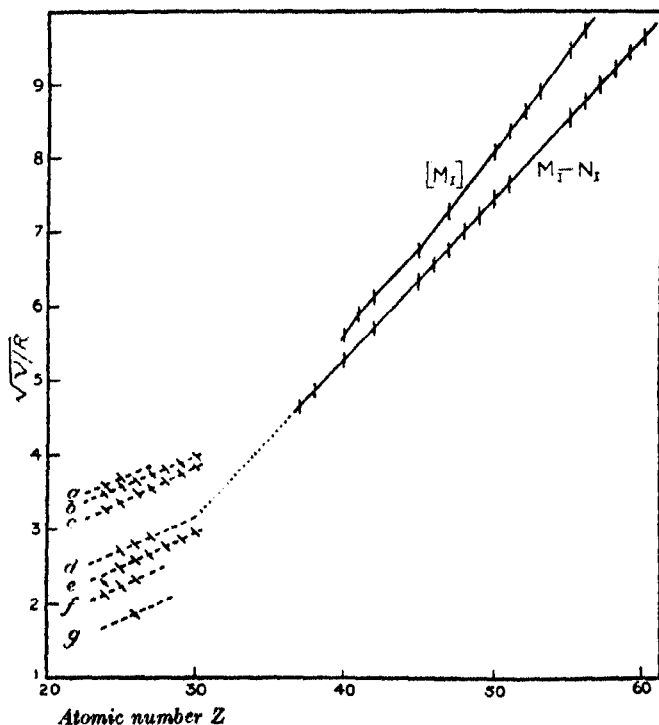


FIG. 12.—\, present research ; | , computed values.

The following considerations enable us to make some test of the correctness of our interpretation of the various critical potentials observed. The wave-numbers of the lines of an optical series are given to a fair degree of approximation by a relation of the form  $\nu = A - R/(m + \alpha)^2$ . In this expression  $A$  and  $\alpha$  are constants, the latter being less than unity,  $R$  is the Rydberg constant, and  $m$  has successive integral values. The radiation of wave-number  $\nu$  is emitted as the result of the transition of an electron from an orbit characterized by the quantity  $R/(m + \alpha)^2$  to an orbit characterized by the

quantity  $A$ . These quantities are measures of the amounts of energy required to ionize the atom by displacing the electron from the orbit concerned and completely removing it from the atom.

In general, the relation connecting the various lines of any particular X-ray series of an element is not as simple as this, but a similar relation to the one given above might be expected to hold good for the wave-numbers associated with electron transitions from virtual orbits, characterized by a particular value of the azimuthal quantum number, to some definite X-ray orbit. Therefore, we might expect the amounts of energy required to transport an electron in any atom from a particular X-ray orbit to various virtual orbits, all having the same azimuthal quantum number, to be such as would give a linear relation between  $\nu/R$  and  $1/(m + \alpha)^2$ . Hence, if the value of the quantity  $\alpha$  were known, it would be possible by plotting the values of  $\nu/R$  corresponding to the observed critical potentials for any element, against suitable values of  $1/(m + \alpha)^2$ , to decide which of the critical potentials are associated with transitions from one level, and which with transitions from a different level. As  $\alpha$  is not known, this cannot actually be done. Nevertheless, some check on our interpretation of our results can still be obtained by plotting the values of  $\nu/R$  corresponding to the observed critical potentials against the reciprocals of the squares of successive integers.

The results obtained for the element iron are shown in fig. 13, which is drawn in the following way:—Values of  $\nu/R$  are taken as ordinates and values of

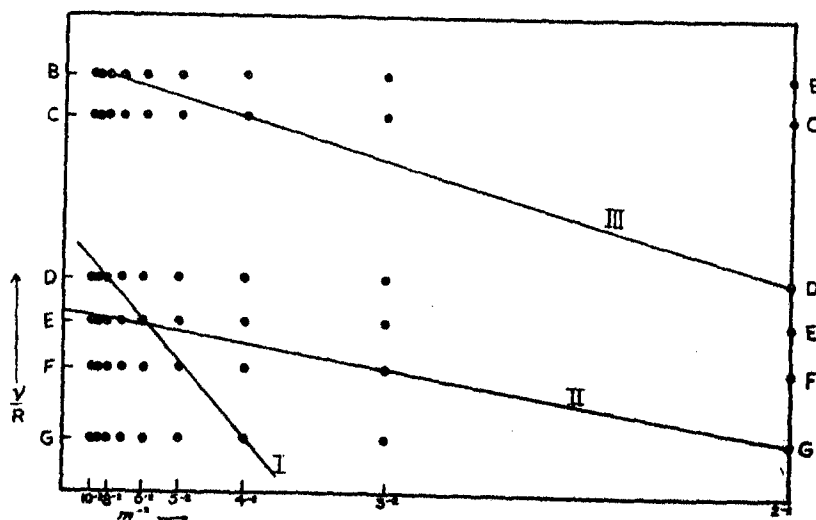


FIG. 13.

$1/m^2$  as abscissæ. Each value of  $\nu/R$  is plotted for values of  $m$  from 2 to 10, and is marked as a ringed point. From the relation  $\nu/R = A/R - 1/(m + \alpha)^2$ , it is at once clear that the larger values of  $\nu/R$  must correspond to the larger values of  $m$ , and it may be seen from the figure that without having recourse to large values of  $m$  (corresponding to the more remote virtual orbits), no line sloping in the required manner can be drawn to pass through, or approximately through, six points, one on each of the lines BB, CC, DD, etc., corresponding to the  $\nu/R$  values for iron ( $z = 26$ ) shown on the series of parallel dotted lines  $b, c, d$ , etc., in fig. 11.

The lines II and I in fig. 13 show that the  $g, f$ , and  $e$  values, and possibly the  $d$  value, may reasonably be associated with transitions from the same electron group,  $M_{I, III}$ , whereas the  $b$  and  $c$  values must correspond to transitions from another electron group,  $M_I$ . The line III shows that the  $d, c$ , and  $b$  values for iron may reasonably be associated with transitions from one group, since points on the three lines DD, CC, and BB can be fitted on to a straight line without using only the larger values of  $m$ . The fact that the  $d$  value can reasonably be connected either with the  $b$  and  $c$  values or with the  $e, f$ , and  $g$  values can be explained on the view that the amount of energy required to remove an electron from an orbit associated with the  $M_{II, III}$  level to a relatively remote virtual orbit is comparable with the amount of energy required to remove an electron from an orbit associated with the  $M_I$  level to the periphery.

In testing the critical potentials for the other elements in the same way, the  $\nu/R$  values of the difference  $M_{III} - N_{II, III}$  were used to correspond to the  $g$  value for iron, and it was found that conclusions similar to those described for iron could be drawn. The  $a$  value, measured only in the cases of manganese and chromium, could be fitted, for each of these elements, on to a line similar to III in fig. 13, thus indicating that this value for each metal may reasonably be associated with a transition from the  $M_I$  level to a virtual orbit. Such evidence as may be obtained from considerations of this nature, therefore, supports the interpretation of the critical potentials already suggested, namely, that the  $a, b, c$ , and  $d$  values are associated with the  $M_I$  level, and the  $e, f$ , and  $g$  values with the  $M_{II, III}$  level.

We have shown that the change in slope of the Moseley lines in the region of the elements under consideration indicates that the development of the  $M$  group is in progress at this stage in the Periodic Table. It does not, however, appear to be possible, from the results obtained, to make any further deductions as to the stages in the development of the sub-groups, since there seems no



means of determining by this method of experiment whether the various critical potentials we have measured are associated with corresponding electron transitions in the different elements ; whether, for instance, the  $c$  values do all correspond to transitions to virtual orbits having the same  $n_k$  in all the elements. The fact that it has been possible to draw in fig. 11 a series of roughly parallel straight lines each passing so nearly through points for the different elements suggests that this is the case, but, on the other hand, the slight deviations of some of the points from the line  $c$  and the line  $e$  respectively, may be attributable to the fact that the values we have connected by the dotted lines do not all correspond to quite the same transitions in different elements.

If the values of the actual potentials for the ionization of the atom by the detachment of an electron from the different sub-groups had been measured, then deviations of points from the corresponding Moseley lines would have had a definite significance. In view, however, of the uncertainty mentioned above, the results do not enable us to draw any definite conclusions with regard to the details of the final constitution of the M group. We cannot, for instance, discriminate from the results of our experiments between Bohr's view of this constitution and the view of Smith\* and of Stoner,† according to which the additional ten electrons which enter the M group between scandium and copper all describe orbits associated with the levels  $M_{IV}$  and  $M_V$ .

Bohr considered the possibility of the removal of electrons from inner groups to an incomplected group of electrons or to virtual orbits, at absorption, and he came to the conclusion that the amount of energy required to bring about a transition to an incomplected group would, in general, differ very little from that required to remove the particular electron completely from the atom. The interpretation of the experimental results of the present investigation, put forward in the foregoing pages, involves the conclusion that, as regards transitions of electrons from the M sub-groups in the region of atomic numbers from 24 to 30, the difference between the amount of energy required to remove an electron from one of these sub-groups to the periphery, and that required to remove it completely from the atom is considerable, and is an appreciable fraction of the latter.

The ratio of the amount of energy required to remove an electron from any given electron group to the periphery, to the amount of energy required to remove the same electron completely from the atom, will be greater the heavier the element, because the particular level under consideration will be more

\* J. D. M. Smith, 'Chemistry and Atomic Structure' (1924).

† E. C. Stoner, 'Phil. Mag.', vol. 48, p. 719 (1924).

deeply seated in the atoms of the heavier elements. Also for a given element the ratio is likely to be greater the more deeply seated the electron group under consideration. We may therefore expect the two quantities of energy to differ by a much bigger percentage in the case of an electron group near the boundary of a light atom, than for a deeply seated group in a heavy atom. As the elements under consideration in this investigation are relatively light, and as the M group is near the boundary of the atom in these elements, the results obtained in the present research are not incompatible with Bohr's general conclusions.

A brief reference to some measurements by Robinson\* may be of interest in this connection. Robinson determined the values of the various energy levels in different atoms by exposing the element under consideration to X-rays of known frequency (the  $K_{\alpha}$  rays of copper), and the paths of the electrons liberated from the element by photoelectric action of the incident X-radiation were bent by a uniform magnetic field on to a photographic plate. From the positions of the lines on the plate the velocities of the various groups of photoelectrons could be determined. The energy of the level within the atom of the element under consideration, from which the electrons had come could then be determined from the relation  $\frac{1}{2}mv^2 = h\nu - W$ , where  $\nu$  is the frequency of the incident radiation and  $W$  the energy of the level. Clearly the energy determined in this way must be that required to remove an electron of an inner group completely from the atom.

A comparison of the results obtained by Robinson with the results obtained by other methods and with Bohr's and Coster's computed values shows that the agreement is very much better for the more deeply seated levels in atoms than for those nearer the boundary. For instance, for the heaviest elements investigated, uranium ( $z = 92$ ) and thorium ( $z = 90$ ) the agreement is quite good for the M levels and for some of the N levels, but Robinson's results for the outermost levels for these elements are consistently higher than the values given by Bohr and Coster. In the case of strontium ( $z = 38$ ), Robinson's values for the L levels are again higher than the computed values. Similarly the  $M_{II, III}$  value for copper ( $z = 29$ ) is definitely higher than Bohr's and Coster's value.

It appears from these results, that for the levels nearer to the boundary of the atom, appreciably more energy is required for ionization than for the removal of the electron to the periphery. These considerations are thus in accord with the views we have put forward.

\* H. Robinson, 'Roy. Soc. Proc.,' A, vol. 104, p. 455 (1923), and 'Phil. Mag.,' vol. 50, p. 241 (1925).

## 90 *Soft X-ray Absorption Limits of Certain Elements.*

The authors desire to acknowledge their indebtedness to the Government Grant Committee of the Royal Society for the means of purchasing some of the apparatus and materials used in this research.

### *Summary.*

Investigations have been made of the voltages corresponding to the critical values of the electron energy associated with some of the longer wave-length absorption stages of the seven successive elements, chromium, managanese, iron, cobalt, nickel, copper, and zinc. The following values, in volts, have been obtained :—

For chromium..	..	60	70	143	160	173
.. manganese	..	68	83	100	152	174
.. iron	.. .. 47	73	90	106	166	181
.. cobalt	.. ..		94	113	171	191
.. nickel	.. ..		104		178	196
.. copper	.. ..		112		193	206
.. zinc	.. ..		119		200	214

The view is put forward, and evidence is deduced to support it from comparisons of measured absorption limits and emission lines, that the generally accepted value of an absorption limit, obtained by spectroscopic methods, corresponds not to ionization of the atom by the detachment from it of an electron in the sub-group concerned, but to the transportation of the electron from the sub-group to the periphery of the atom, *i.e.*, to the levels of the most loosely bound electrons. For the more deeply seated levels within atoms, the quantity of energy required to move an electron to the periphery probably differs by a very small proportion from that required to effect its complete detachment from the atom. In the case of levels near the normal boundary of the atom the two quantities may, however, differ by a much larger proportion, giving the possibility of detection of absorption stages corresponding to transitions to virtual orbits between the periphery and the region at which the electron may be considered to be detached from the atom, and the latter ionized.

Extrapolation of the Moseley curves for the various absorption limits down to low atomic numbers shows that the values obtained in this investigation must be associated with absorption of energy by electrons in the M sub-groups. The several values obtained for each element are attributed to selective absorption stages resulting in the transference of electrons from the sub-groups associated with the levels  $M_I$  and  $M_{II, III}$  to various virtual orbits outside the normally occupied region of the atom, and not to actual ionization of the atom.

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*Experimental Determination of the Thermal Conductivities  
of Gases.*

By H. GREGORY, B.Sc., D.I.C., and C. T. ARCHER, B.Sc., A.R.C.S., D.I.C.

(Communicated by Prof. H. L. Callendar, F.R.S.—Received May 21, 1925.)

(1) *Introduction.*

The analysis of the dynamic theory of gases has indicated an interesting relation between the viscosity  $\eta$ , the thermal conductivity  $K$ , and the specific heat at constant volume  $C_v$  of a gas. This relation is represented by the expression

$$K = f \cdot C_v \cdot \eta,$$

in which the factor  $f$  depends upon the law of force operative in molecular collision, and is known if  $K$ ,  $C_v$ , and  $\eta$  can be determined experimentally.

In view of its importance in this respect, and also from the fact that great accuracy and consistency of measurement are possible in modern determinations of the viscosity of gases, the importance of the development of a method by which the conductivity can be measured with the same order of accuracy demands increasing attention.

The state of affairs as regards the thermal conduction of gases is emphasized by the fact that the results available for air at 0° C. vary from 0.0000447, as determined by Eckerlein,\* to 0.0000586 cal. cm.<sup>-1</sup> sec.<sup>-1</sup> deg.<sup>-1</sup> C., as determined by Müller.† Also, the mean of the values obtained by 14 observers of  $K_0$  for air is 0.0000522, the average departure from the mean value being about 7 per cent. This extreme inconsistency of the various observers amongst themselves suggests that considerable difficulty is experienced in disentangling the effects due to conduction, convection and radiation, and the experiments to be described have been made with a view to an accurate investigation of these effects under widely varying conditions of temperature and pressure.

With regard to the great difficulty of convection, it is interesting to note that up to the present time it has not been found possible to determine theoretically convective losses of heat, and the usual procedure of regarding such losses to be negligible at a low enough pressure is not susceptible of application where a high order of accuracy is demanded.

\* Eckerlein, 'Ann. der Phys.,' vol. 3, p. 120 (1900).

† Müller, 'Wied. Ann.,' vol. 60, p. 82 (1897).

Further, there is no very exact verification that thermal conduction is independent of pressure over a large range of pressure, as also indicated by the dynamic theory of gases, and, in view of the importance of this question, it has been made the subject of a separate investigation.

The variation of the thermal conductivity of gases with temperature has been considered theoretically by Maxwell,\* Clausius and Chapman,† and experimentally by Eucken,‡ but here again there is extreme inconsistency amongst the results of the various observers. The question is one which involves great sensitivity and very accurate measurement.

## (2) *Previous Determinations.*

All previous investigations of the thermal conduction of gases have been confined to modifications of three principal methods, which we shall consider briefly in historical order :—

(a) The cooling thermometer method, in which a thermometer was allowed to cool in an enclosure, it being assumed that at a pressure of a few millimetres the convective losses of heat were eliminated, was used by Kundt and Warburg.§

(b) The hot-wire method, in which a wire coaxial with a closed cylindrical space filled with the gas under investigation is heated by an electrical current, was first used by Schleiermacher|| to give an absolute value for the conductivity. Here the processes of heat transmission are by (1) convection, which was assumed to be negligible at a low enough pressure, (2) conduction along the leading wires, and (3) radiation, the correction in this case being found by calculation. Stafford¶ and Eucken\*\* also used this method for relative determinations.

Weber,†† in his recent investigation, used this method with an important modification first adopted by Goldschmidt‡‡ in his experiments on the Thermal Conduction of Liquids. In this case the heat conducted along the leading wires was eliminated by the inclusion of an exactly similar, though shorter, tube in the experimental system. The end-effect compensation for the elimina-

\* Maxwell, 'Scientific Papers,' vol. 2, p. 23.

† Chapman, 'Phil. Trans.,' A, vol. 211, p. 433 (1911).

‡ Eucken, 'Phys. Zeit.,' vol. 12 (1911); vol. 14 (1913).

§ Kundt and Warburg, 'Pogg. Ann.,' vol. 156, p. 177 (1875).

|| Schleiermacher, 'Wied. Ann.,' vol. 34, p. 623 (1888).

¶ Stafford, 'Zeit. Phys. Chem.,' vol. 77, p. 86 (1911).

\*\* Eucken, *loc. cit.*

†† S. Weber, 'Ann. der Phys.' (4), vol. 54, p. 342 (1917).

‡‡ Goldschmidt, 'Phys. Zeit.,' vol. 12, p. 418 (1911).

tion of conduction along the leading wires was first applied by Prof. Callendar\* in the construction of platinum thermometers and has been used in all his instruments for the last thirty years. It is particularly important in the measurement of rapidly varying temperatures, as in the cylinder of a steam engine or gas engine. The same principle has since been applied by Prof. Callendar to many other experiments on radiation, conduction, etc., some of which are described in a paper on the Radiobalance.† Unfortunately, the Germans and Americans, not realising the importance of the elimination of conduction along the leading wires until too late, have widely exploited a potentiometer method of measuring resistances of platinum thermometers as being greatly superior to the English method. In point of fact the potentiometer method has no advantage over the Wheatstone bridge method, and is liable in practice to the very great disadvantage that it cannot be used at all for simultaneous differential measurements, which are most important in determinations of specific heat, conductivity and other physical properties. For this reason, the method described in the present paper, though superficially similar, was a vital improvement on that employed by Weber, who was unable to keep the temperature of his wire accurately constant under different conditions, or to investigate the convective losses satisfactorily as explained below. The convective losses were assumed to be eliminated by a vertical disposition of the tubes. Although such losses are certainly less for this disposition than for any other, neither Weber's research nor any other to date has attempted to investigate the convective losses in such a way as to disentangle them correctly from the purely conductive losses. In the authors' opinion this failure has been due to an inadequate variation of the temperature and pressure conditions in conjunction with a consideration of the dimensions of the tubes, and it is along such lines only that any investigation which aims at the correct disentanglement of the effects of conduction and convection can be successful. Radiation losses were allowed for by making use of Knudsen's results on the radiation of bright platinum.

(c) The plate method, which has been fairly successful, was first used by Todd‡ and recently by Hercus and Laby.§ Here the gas under investigation was in the form of a horizontal stratum between plates maintained at constant temperatures, and so arranged that the upper plate was the hotter. In this

\* Callendar, 'Proc. Inst. C.E.,' vol. 131 (1897-8).

† Callendar, 'Proc. Phys. Soc.,' vol. 23 (1910).

‡ Todd, 'Roy. Soc. Proc.,' A, vol. 83, p. 19 (1909).

§ Hercus and Laby, 'Roy. Soc. Proc.,' A, vol. 95, p. 190 (1919).

way convective losses were entirely avoided, but again this disposition involves the greater complication of securing constancy of temperature of the plates, necessitating the construction of guard rings, and the still greater difficulty of the variation of the pressure conditions. In both these investigations the experimenters were able to work at one pressure and one temperature gradient only, and their results are thus valueless from the point of view of the variation of the conductivity with temperature and pressure. The results obtained by Hercus and Laby were somewhat inconsistent as can be seen from the following figures taken from their paper, referring to experiments on air at the same pressure and with the same temperature gradient :—

Experiment.	$K_{22}$ .	Experiment.	$K_{22}$ .
1	0·0000600	5	0·0000572
2	587	6	580
3	580	7	571
4	554	8	564

It will be seen from the above that the departure from the mean value is in one case as much as 5 per cent. The experiments of Todd, although very interesting historically, do not involve the accuracy demanded by modern science in thermal measurements. The upper plate was heated by means of steam and the measurements were thus confined to large gradients of temperature. The heat transmission was measured by a rough calorimetric method, the radiation being eliminated by varying the distance between the hot and cool plates. It will be seen that although an important advance was made in the subject, convective losses being absent, the experimental system was not susceptible of great accuracy and the lowness of the results (*e.g.*, 0·0000499 for air) suggests that there were heat losses not correctly allowed for in the calculation.

### (3) *Principle of the Present Experiments.*

The gas under investigation is confined in a cylindrical tube A (fig. 1) co-axial with which is a platinum wire heated by an electric current and maintained at a constant temperature.

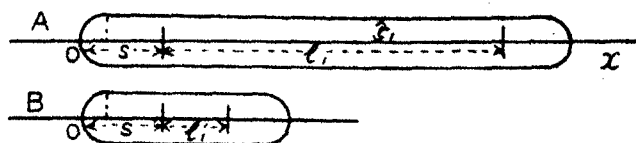


FIG. 1.

Heat passes from the wire to the walls of the tube by Convection and Conduction through the gas, by Radiation, and a certain portion of it by conduction along the leading wires. This process of heat transmission can be represented for any pressure of the gas by the equation :—

$$C^2 R_\theta^{l_1} + 2 \int_0^s C^2 \frac{\rho_\theta dx}{A} = \frac{2\pi K l_1 \theta}{\log_e r_2/r_1} + 2 \int_0^s 2\pi f(x) dx + \phi_1 + \psi_1 + H_1, \quad (1)$$

where  $C$  is the current strength  $R_\theta^{l_1}$ , the resistance of the wire at the temperature  $\theta^\circ \text{C}$ ,  $s$  the length of the wire over which the temperature varies,  $l_1$  the length over which the temperature is constant,  $r_1$  and  $r_2$  the radii of the wire and tube respectively,  $\phi_1$  the convective heat loss,  $\psi_1$  the radiation loss and  $H_1$  the heat conducted along the leading wires. In this equation the integral on the left-hand side represents the development of heat in a wire of length  $s$  whose temperature varies according to some known function of  $x$ , and that on the right-hand side the loss of heat by conduction from the same length of wire.

If we have an exactly similar tube  $B$  in gaseous connection with  $A$ , but differing from  $A$  in length only and heated by the same electric current, then for  $B$  can be written

$$C^2 R_\theta^{l_1'} + 2 \int_0^s C^2 \frac{\rho_\theta dx}{A} = \frac{2\pi K l_1' \theta}{\log_e r_2/r_1} + 2 \int_0^s 2\pi f(x) dx + \phi_1' + \psi_1' + H_1', \quad (2)$$

in which the dashed symbols refer to the shorter tube  $B$ .

If, now, we can assume that the heat conducted along the leading wires is the same in both cases, and if, also, the distribution of temperature is the same along both wires, then, from (1) and (2) by subtraction

$$C^2 (R_\theta^{l_1} - R_\theta^{l_1'}) = \frac{2\pi K (l_1 - l_1') \theta}{\log_e r_2/r_1} + (\phi_1 - \phi_1') + (\psi_1 - \psi_1') \quad (3)$$

which can be written

$$C^2 R = \frac{2\pi K l \theta}{\log_e r_2/r_1} + \phi + \psi. \quad (4)$$

Equation (4) represents, if our assumptions are true, that we can focus our attention on an isolated portion of the wire of length  $l$  or  $(l_1 - l_1')$  which is of uniform temperature throughout its length.

It can be shown theoretically that the heat conducted along the leading wires is the same for both tubes, to a very high order of accuracy.

Consider the ideal case of a wire stretched between two metal electrodes at a



temperature of  $0^\circ \text{C.}$ , heated by an electric current of strength  $C$  and surrounded by a coaxial tube of radius  $r_2$ .

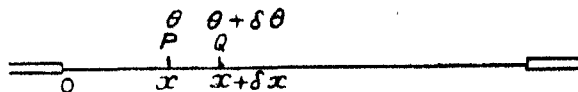


FIG. 2.

Let the length of the wire be  $2l$  and its area of cross-section  $A$ . Let  $\theta$  be the temperature at a point  $P$  on the wire distant  $x$  from a point  $O$  taken as origin, and  $\theta + \delta\theta$  the temperature at  $Q$  distant  $x + \delta x$  from  $O$ .

Then, for the thermal equilibrium of the element of wire  $PQ$  we have

$$\delta x \cdot KA \frac{d^2\theta}{dx^2} + \frac{C^2 \rho_\theta \delta x}{JA} = \frac{2\pi K_g \theta \cdot \delta x}{\log_e r_2/r_1}$$

where  $\rho_\theta$  is the specific resistance of the material of the wire at a temperature  $\theta^\circ \text{C.}$ ,  $K$  the thermal conductivity of the material of the wire,  $r_1$  the radius of the wire, and  $K_g$  the thermal conductivity of the gas surrounding the heated wire, *i.e.*,

$$\frac{d^2\theta}{dx^2} + \frac{C^2 \rho_0 (1 + \alpha \theta)}{J \cdot KA^2} = \frac{2\pi K_g \theta}{KA \log_e r_2/r_1}$$

where  $\rho_0$  is the specific resistance of the material of the wire at  $0^\circ \text{C.}$  and  $\alpha$  the coefficient of increase of resistance of the wire.

This equation is of the type

$$\frac{d^2\theta}{dx^2} - P \cdot \theta = -Q,$$

where

$$P = \frac{2\pi K_g}{KA \log_e r_2/r_1} - \frac{C^2 \rho_0 \alpha}{J \cdot KA^2}$$

and

$$Q = \frac{C^2 \rho_0}{J \cdot KA^2},$$

and the solution is given by

$$\theta = \frac{Q}{P} + C_1 \cdot e^{\sqrt{P} \cdot x} + C_2 \cdot e^{-\sqrt{P} \cdot x}, \quad (5)$$

where  $C_1$  and  $C_2$  are constants which can be found from the boundary conditions,  $\theta = 0$  when  $x = 0$  and when  $x = 2l$ , and

$$C_1 = -\frac{Q}{P(1 + e^{2\sqrt{P} \cdot l})},$$

$$C_2 = -\frac{Q \cdot e^{2\sqrt{P} \cdot l}}{P(1 + e^{2\sqrt{P} \cdot l})}.$$

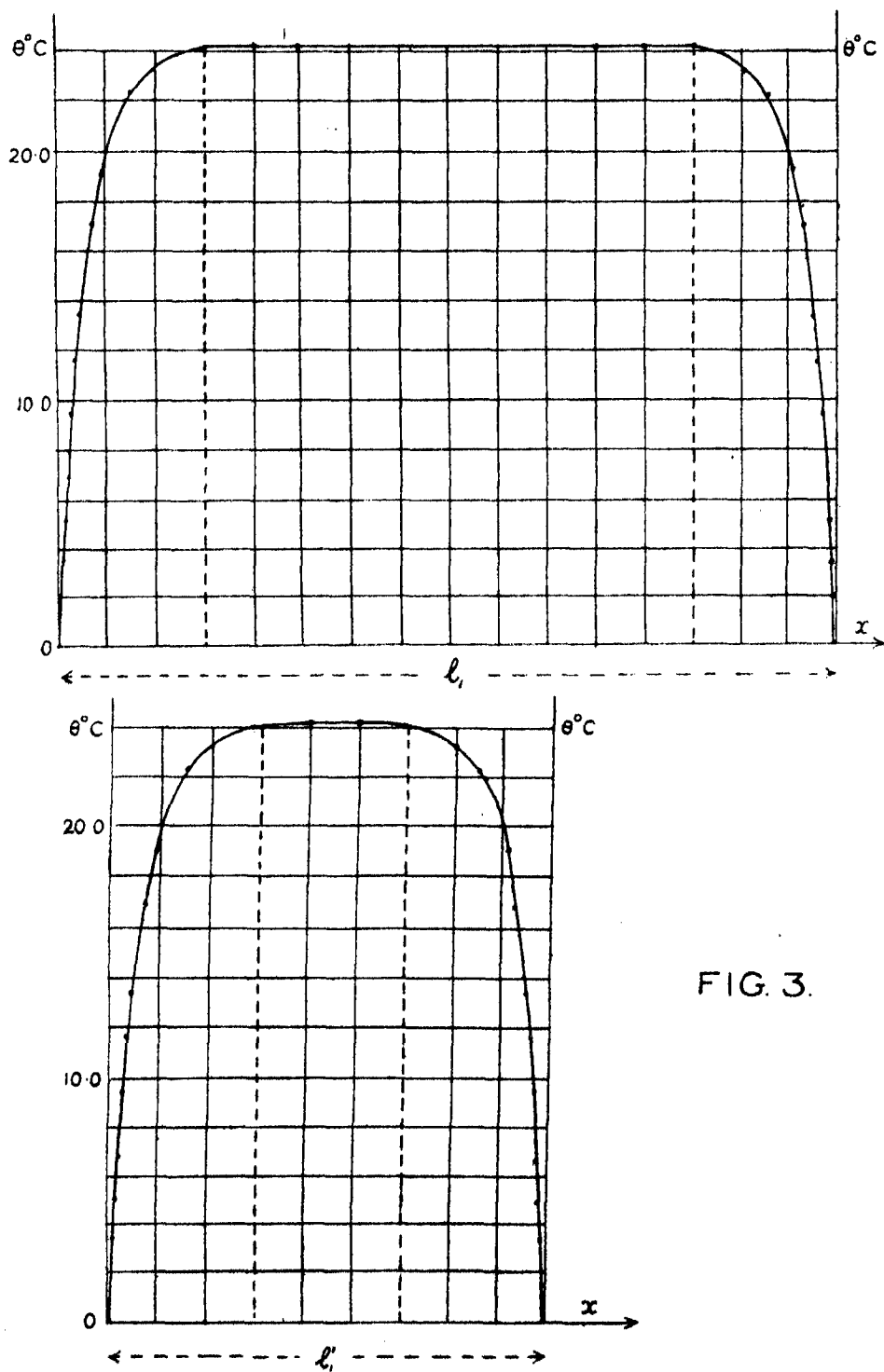


FIG. 3.

Since the value of  $e^{2\sqrt{P} \cdot l}$ , calculated for the wires and tubes used, is large compared with unity, (5) can therefore be written

$$\theta = \frac{Q}{P} (1 - e^{-\sqrt{P} \cdot x} - e^{-\sqrt{P} \cdot (x-2l)}). \quad (6)$$

The above formula (6) has been used to calculate the variation of temperature along the wire for particular cases, the result being shown graphically in fig. 3, indicating that the distribution of temperature along the wires is the same for both the main and compensating tubes as used in the experimental system.

Now, when the wire has reached the steady state, the heat flowing from the wire to the electrode is given by

$$KA \left( \frac{d\theta}{dx} \right)_{x=0} = \frac{QKA}{\sqrt{P}} (1 - e^{-\sqrt{P} \cdot 2l}),$$

which indicates that the heat conducted from the wire along the leading wires is a function of the length of the wire, and is the same for lengths of wire as used in the main and compensating tubes of the experimental system to be described, since  $e^{-\sqrt{P} \cdot 2l}$  is of zero value for values of  $l$  greater than 4 cms.

The principle of the compensation of the heat flowing along the leading wires and of the equality of the distribution of temperature along the long and short wires is thus established in the presence of a gas. If, now, the tubes A and B (fig. 4) are made to form the main and compensating arms, respectively, of a Callendar-Griffiths bridge, it is seen that, as far as the measurement of

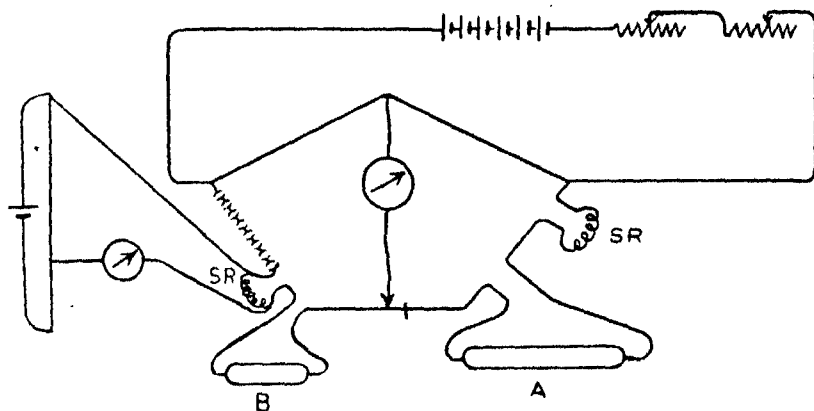


FIG. 4.

resistance is concerned, we are dealing with an isolated portion of platinum wire of length  $l$ , and such that if any current is passed through the circuit and

the bridge is balanced, then the effective wire is uniform in temperature throughout its length  $l$ .

Briefly, the ideal procedure is as follows :—

The resistance of the effective length of wire is determined at the temperature of steam and of melting ice, by surrounding the tubes A and B with the appropriate bath. The fundamental interval of the wire having been determined, it is possible to set the bridge contact in such a position that the wire will be at a known temperature, corresponding to a known gradient of temperature between the wire and the walls of the tubes. This gradient can then be maintained by varying the strength of the current flowing in the bridge, using rheostats specially constructed for the purpose, it being necessary, of course, to maintain the external temperature of the walls of the tubes at a constant value. The gas under investigation is then subjected, in a manner to be described below, to a variation of pressure conditions. This will involve generally a change in the current strength necessary to maintain the balance of the bridge, these changes in the strength of the current being measured by means of a potentiometer, using standard resistance coils in series with the tubes and the coils of the bridge.

Before describing the construction of the apparatus and the experimental procedure in detail, it will be necessary to consider the manner in which the convective and radiation losses of heat from the wire are separated from that due purely to conduction.

#### (4) *Elimination of Convection.*

The difficulties of successfully allowing for the convective losses in determining the thermal conduction are enhanced by the still greater difficulty of investigating such losses from a theoretical standpoint. Previous experimenters using the hot-wire method have been content to assume that by lowering the pressure sufficiently convective losses have been obviated.

It will now be shown that by using two separate compensating systems of tubes identical in all respects except that of their radii, it is possible to find, to a high degree of accuracy, the pressure in both tubes at which the convective losses vanish. These pressures will generally be different for each tube and may be denoted by  $p_N$  for the narrow tube and  $p_W$  for the wide.

The quantities

$$\frac{C_W^2 R_2 \log_e r_2/r_1}{2\pi J l \theta} \quad \text{and} \quad \frac{C_W^2 R_3 \log_e r_3/r_1}{2\pi J l \theta}$$

will be termed the equivalent conductivities,  $K_N$  and  $K_W$ , of the gas for the narrow and wide tubes, respectively, at any pressure. Now, at the pressures  $p_N$  and  $p_W$ , these are equal to each other and to the absolute conductivity of the gas, assuming that  $K$  is independent of pressure, an assumption which has been verified experimentally by the authors to a high degree of accuracy and forms the subject of a separate paper. Hence,

$$\left( \frac{C_W^2 R_0 \log_e r_2/r_1}{2\pi J l \theta} \right) p_N = \left( \frac{C_N^2 R_0 \log_e r_3/r_1}{2\pi J l \theta} \right) p_W = K,$$

i.e.,

$$\frac{C_N^2}{C_W^2} = \frac{\log_e r_3/r_1}{\log_e r_2/r_1} = \alpha,$$

where  $\alpha$  is a constant which can be determined accurately from the dimensions of the tubes and wires.

The above relation is an important one in the accurate determination of the absolute conductivity of the gas, since it enables us to fix with a high degree of accuracy the pressures at which the convective losses disappear as the pressure is varied. This test will now be considered graphically.

Let the curves (fig. 5) denote the variations of  $K_N$ ,  $K_W$ ,  $C_N^2$  and  $C_W^2$  with pressure.

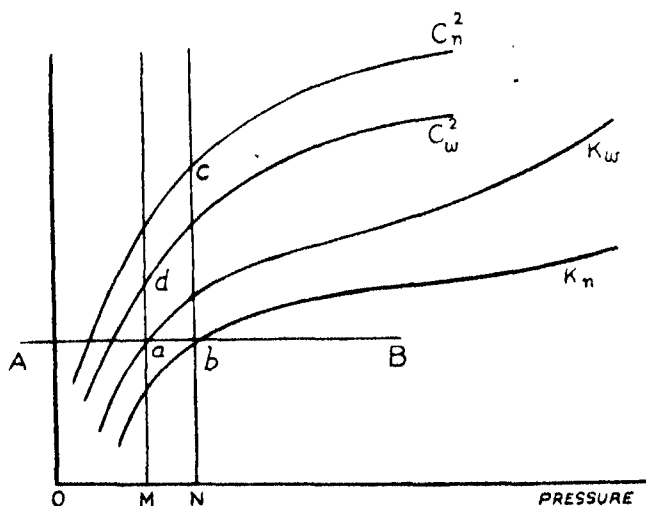


FIG. 5.

Draw the line AB parallel to the pressure axis cutting the curves  $(K_N, p)$ ,  $(K_W, p)$  in  $b$  and  $a$ , respectively. Let the point  $b$  correspond to  $p_N$  and the point  $a$  to  $p_W$ .

If now parallels to the  $C^2$  axis are constructed through  $b$  and  $a$  cutting the  $C_N^2$  and  $C_W^2$  curves in  $c$  and  $d$ , and if we assume that the points  $a$  and  $b$  represent the points on each curve where the convection vanishes, then

$$Ma = Nb = K,$$

and also

$$\frac{Nc}{Md} = \frac{(C_N^2)^2}{(C_W^2)^2} = \frac{\log_e r_3/r_1}{\log_e r_2/r_1} = \alpha.$$

Hence, corresponding to any set of observations, the following construction will indicate the points  $a$  and  $b$  :—

Draw a series of parallels to the pressure axis, and through the points at which they intersect the  $K_N$  and  $K_W$  curves construct parallels to the  $C$  axis cutting the two curves in points  $c_1, c_2, c_3$ , etc., and  $d_1, d_2, d_3$ , etc. Two of these points and two only will satisfy the condition

$$(C_N^2)^2/(C_W^2)^2 = \alpha$$

and  $K$  is then known.

It will be remembered that the procedure for the elimination of the convective losses of heat is dependent for its success on how accurately the wire can be maintained at a constant temperature during the variation of the pressure conditions in the tubes, and it might be pointed out at this stage that such maintenance of constant temperature would be experimentally impossible with any system other than a bridge system such as that used in this investigation. Previous observers using the hot wire method have adopted a potentiometer system of measurement in which it was not possible to maintain the wire at a constant temperature throughout an experiment. Taking an example from the work of S. Weber on the conductivity of Air,\* the wire temperature varied more than 2 per cent., during the reduction of the pressure from 75.57 cm. to 0.57 cm., while in the present investigation there was no variation in the temperature of the wire, and in the gradient of temperature between the wire and the outside bath the greatest variation was not more than 1 part in 2,000. The method adopted in the present work aims not only at a disentanglement of the convective losses of heat, but also claims an accurate quantitative investigation of such losses and their variation with temperature and pressure.

#### (5) Radiation.

It has been stated by Knudsen and others, as a result of experimental work, that the Radiation from bright platinum varies as the fifth power of the absolute temperature of the wire.

\* S. Weber, *loc. cit.*

In the present case, we are concerned with the energy loss by radiation from a bright platinum wire in an enclosure filled with a gas, and for the present purpose it will be assumed that such purely radiation losses will be the same for the same temperature of the wire if the enclosure is evacuated. This brings us to an important point, viz., can it be assumed that the temperature distribution along the long and short wires is the same in the presence of a gas as in a vacuum? If such is the case, the problem is one simply of obtaining a high vacuum and following the same experimental procedure as described for a gas, in which case the loss of heat by radiation from the wire of equivalent length  $l$  is to be investigated. In any case, since such radiation loss forms only a small proportion, less than 1 per cent., of the total heat losses by conduction, and since an error of 20 per cent. in the measurement of such radiation would affect the calculated value of the thermal conductivity only to the extent of 1 in the third figure, i.e., an error of 1 in 500, we need not concern ourselves with the problem of the temperature distribution in the same strict detail as has been observed for the case when a gas was present. It may be mentioned, however, that such temperature distribution is not quite the same for an evacuated enclosure as in the presence of a gas, and, generally speaking, the less the loss of heat from the wire the greater the distance from the end of the wire necessary to reach constant temperature in the wire. Hence for hydrogen and other gases of higher conductivity this distance will be less than for air, and the higher the conductivity the more ideally perfect is the present method of compensating for the loss of heat along the leading wires.

Having satisfied the temperature distribution conditions in this case, we are faced with the difficulties of attaining and maintaining a high vacuum in the tubes. It will be seen that since the conductivity of a gas persists with little diminution, even at pressures of the order of 1 mm., and is very large compared with the radiation loss, it is of little use attempting to obtain the required vacua with pumps alone. After much experimental work on the subject it was found necessary to supplement the pumps by the use of glass pockets (in gaseous connection with the enclosure) filled with cocoanut charcoal and immersed in liquid air in order to obtain sufficiently high vacua.

Having obtained a vacuum of the required order, a small current, the approximate magnitude of which had been determined previously by trial experiments, was passed through the two systems of tubes, and, allowing time for the steady state to be reached, the bridges were balanced in turn, the current also being measured immediately by the potentiometer. This process was then repeated, using three other slightly larger currents.

Finally, a similar series of observations was made with the tubes surrounded by steam instead of ice-water.

From the balance points of the bridges the temperature of the wire in each tube system for each current was calculated, and thence the resistance per unit length of the wire at each temperature. Finally, the total heat loss from the wire in each case was calculated, using this resistance and the corresponding value of the current given by the potentiometer.

The results obtained are shown in the following tables, the wire temperature being given in degrees Centigrade :—

(a) Temperature of bath, 0° C.

Current.	Narrow Tubes.			Wide Tubes.		
	Wire Temp.	R/l	Heat Loss (cal./cm.).	Wire Temp.	R/l	Heat Loss (cal./cm.).
0.0146	3.685	0.05381	$274 \times 10^{-8}$	4.456	0.05397	$275 \times 10^{-8}$
0.0219	8.665	0.05485	$629 \times 10^{-8}$	9.959	0.05511	$632 \times 10^{-8}$
0.0288	15.472	0.05625	$1115 \times 10^{-8}$	16.598	0.05649	$1120 \times 10^{-8}$
0.0406	31.532	0.05958	$2351 \times 10^{-8}$	32.914	0.05987	$2356 \times 10^{-8}$

(b) Temperature of Bath, 99.155° C.

Current.	Narrow Tubes.			Wide Tubes.		
	Wire Temp.	R/l	Heat Loss (cal./cm.).	Wire Temp.	R/l	Heat Loss (cal./cm.).
0.0172	102.161	0.07400	$523 \times 10^{-8}$	102.448	0.07406	$524 \times 10^{-8}$
0.0232	104.573	0.07451	$958 \times 10^{-8}$	105.089	0.07459	$959 \times 10^{-8}$
0.0332	109.996	0.07558	$1991 \times 10^{-8}$	110.853	0.07575	$1995 \times 10^{-8}$
0.0462	119.951	0.07758	$3956 \times 10^{-8}$	120.930	0.07777	$3966 \times 10^{-8}$

Curves were drawn plotting the total heat loss per unit length of wire against the temperature of the wire. These curves are shown in figs. 6 and 7.

It might be pointed out that in the case of the above results, the total heat loss in the wide tubes is less in every case than in the narrow tubes for the same temperature of the wire. This difference can be attributed to residual gas effects due to the extreme difficulty in obtaining high vacua. As the pressure is reduced in both systems of tubes simultaneously, a point will be reached when the mean free path of the molecules will be comparable with the distance between the wire and the wall of the tube, and on this account the



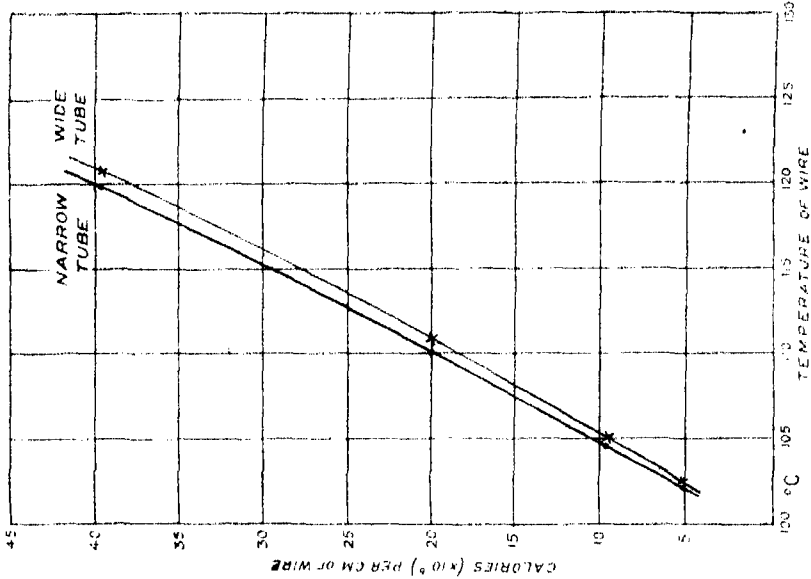


Fig. 7.

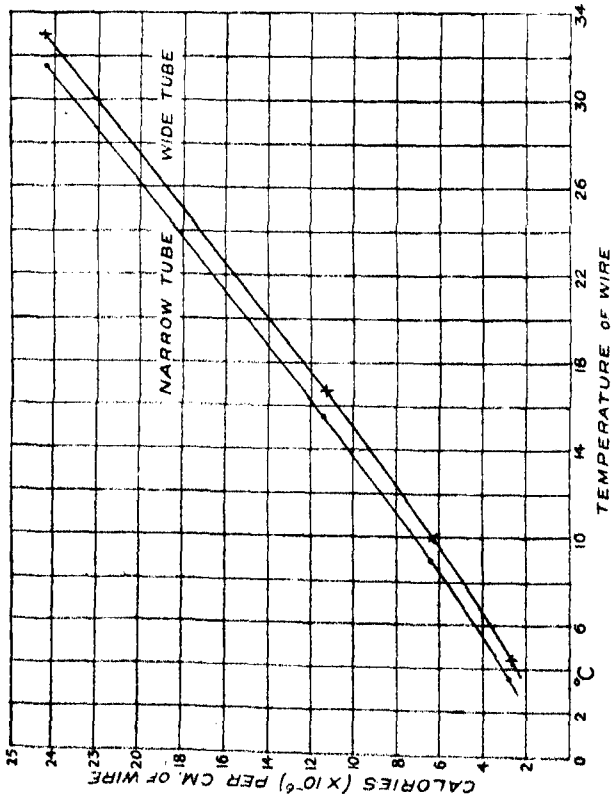


Fig. 6.

conductivity will cease to be independent of pressure, but will vary with the pressure in a perfectly definite manner. The stage at which this effect will first become operative will occur at a higher pressure in the narrow tube system. This is shown up very clearly by the experimental results embodied in figs. 10 and 11 (pp. 113 and 118) for air and hydrogen respectively.

Now, it has been shown experimentally by Soddy and Berry\* and Knudsen† that at pressures within the range of those existing in the best vacua obtainable, the conductivity of a gas is proportional to the pressure, and for this reason the residual conductivity will be the same at such pressures for both systems of tubes.

If  $W_N$  and  $W_W$  represent the total heat loss per cm. of wire and  $K_R$  the residual conductivity of the gas at the partial vacuum used, then for the same temperature of the wire in the narrow and wide tube systems we have

$$W_N = \frac{2\pi K_R \theta}{\log_e r_2/r_1} + \phi_\theta \quad (1)$$

and

$$W_W = \frac{2\pi K_R \theta}{\log_e r_3/r_1} + \phi_\theta, \quad (2)$$

where  $\phi_\theta$  is the loss of heat by radiation at a temperature  $\theta$  of the wire.

Eliminating  $K_R$  from (1) and (2),  $\phi$  can be calculated for the temperature  $\theta$  of the wire. In the same way,  $\phi$  can be found at other temperatures of the wire.

It is an interesting point that the variation of  $W_N$  and  $W_W$  with  $\theta$  is most nearly expressed by an equation of the type.

$$W = b \cdot \theta^5 - a,$$

where  $b$  and  $a$  are constants, whereas the values of  $\phi$  as calculated from (1) and (2) are not in accordance with such a variation, but are for the range of temperatures used above more nearly linear with the temperature of the wire. This seems to indicate that the fifth-power law holds only for the compounded heat loss by radiation and residual conduction through the gas.

The corrections used for radiation in conjunction with the results for atmospheric air and hydrogen are shown at the head of the tables below.

\* Soddy and Berry, 'Roy. Soc. Proc.,' A, vol. 83, p. 254 (1909).

† Knudsen, 'Ann. d. Phys.,' vol. 34, p. 593 (1911).

(6) *Correction for Glass Wall.*

In the equation which has been derived for the transmission of heat by conduction and convection from a hot wire coaxial with a cylindrical glass tube

$$\frac{C^2 R}{l} = \frac{2\pi K \theta}{\log_e r/r_1} + \phi,$$

it is understood that  $\theta$  refers to the temperature difference between the wire and the internal surface of the glass tube. In order to calculate the conductivity of the gas, it will be necessary to determine the temperature drop across the wall of the tube.

We can write

$$\theta = \theta_1 - \theta_2,$$

where  $\theta_1$  is the difference of temperature between the wire and the bath and  $\theta_2$  is the temperature drop across the glass wall. This correction which varies with the nature of the gas under investigation and also with the nature of the glass used will now be considered.

Let  $r_4$  and  $r_6$  denote the external radii of the narrow and wide tubes respectively, and  $W_N$  and  $W_W$  the total heat loss per cm. of wire in each tube system.

Then we can write

$$W_N = \frac{2\pi K_g (\theta_1 - \theta_2)}{\log_e r_4/r_2} = \frac{2\pi K_g \theta_N}{\log_e r_4/r_2}$$

and

$$W_W = \frac{2\pi K_g (\theta_1 - \theta_3)}{\log_e r_6/r_3} = \frac{2\pi K_g \theta_W}{\log_e r_6/r_3},$$

$\theta_N$  and  $\theta_W$  denoting the difference of temperature between the inner and outer surfaces of the glass wall of the narrow and wide tubes respectively, and  $K_g$  the thermal conductivity of the glass. These equations, if  $K_g$  is known, enable us to calculate the temperature corrections due to this effect, i.e.,

$$\theta_N = \frac{W_N \log_e r_4/r_2}{2\pi K_g}$$

and

$$\theta_W = \frac{W_W \log_e r_6/r_3}{2\pi K_g}.$$

It will be shown that the order of this correction is in the case of hydrogen about 1 per cent. of the temperature gradient across the gas in the narrow-tube system.

In view of the fact that the glass used in the apparatus (Whitefriars Flint glass, supplied by Messrs. James Powell & Sons, Ltd.) was of a composition such that its thermal conductivity was not known with any exactness, it was considered worth while making this determination the subject of a separate investigation in which the thermal conductivity of the actual material in the tube form was measured. The work is described in a separate paper.

Thus, if  $\theta$  denotes the difference of temperature between the wire and the bath surrounding the tubes, then the temperature gradient across the gas can be written

$$\theta = \theta_N \text{ for the narrow tube system,}$$

and

$$\theta = \theta_W \quad \text{,,} \quad \text{wide} \quad \text{,,} \quad \text{,,}$$

in which  $\theta_N$  and  $\theta_W$  can be calculated.

#### (7) Construction of Apparatus.

In the construction of the apparatus used in the experimental work extreme care was taken both in the choice of material and also in the measurement of the dimensions of the apparatus.

The dimensions of the tubes and wires are shown :—

	Narrow.	Wide.
Internal radius of tube ( $r_2$ ) .. ..	0.4592 cm. ( $r_3$ )	1.1714 cm.
External .. .. ( $r_4$ ) .. ..	0.5215 cm. ( $r_5$ )	1.2360 cm.
Thickness of wall .. ..	0.0623 cm.	0.0646 cm.
Radius of platinum wire .. ..	( $r_1$ ) 0.007696 cm.	
.. .. leading wires .. ..	0.02829 cm.	

*Arrangement of Apparatus.*—The completed tubes were next assembled in gaseous connection with each other, and with the remainder of the apparatus as shown in the diagram, fig. 8, the tubes being arranged in as small a space as possible, but yet to permit of a good circulation round them of the liquid contained in the bath. One exit tube, provided with a tap, was connected to a drying chamber containing phosphorus pentoxide, and thence to the gas supply. The other exit tube was connected to a charcoal pocket (D), the U-tube pressure gauge (E), a Toepler gas recoverer (F), a discharge tube (G) and a McLeod pressure gauge (H), an outlet tube with tap (K) also being attached to connect with the vacuum pumps. The whole was made as compact as possible and mounted on suitable stands, the tubes themselves being fixed to the cover of the bath used to maintain a constant temperature

outside the tubes. This bath consisted of a copper tank, about  $60 \times 15 \times 18$  cms., mounted in an iron framework and well lagged with asbestos wool and asbestos board. The cover of the bath was of wood, the lower face being lined with sheet copper flanged to fit the tank, holes being bored for the connecting wires, and larger holes to allow the introduction of water, ice, etc., into the tank and to permit the use of stirring apparatus.

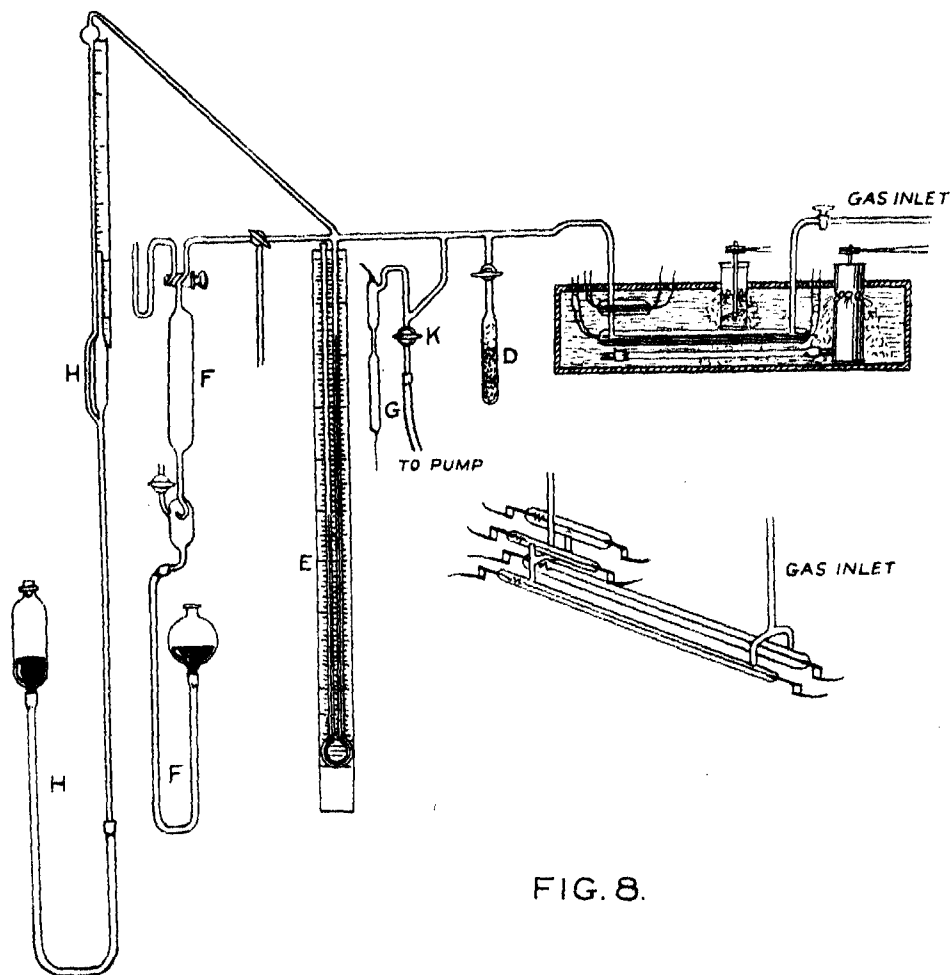


FIG. 8.

FIG. 8.

*Electrical Apparatus.*—The arrangement of the electrical apparatus and the scheme of connections are shown in diagrammatic form in fig. 9. Each pair of tubes was connected in a self-contained circuit separate from the other

pair with the sole exception that the same galvanometer (L), a very sensitive moving coil instrument, was used in both circuits, a mercury key (M) being arranged so that it could be switched into either circuit at will. The long tube was connected in series with a standard 1-ohm resistance coil in oil bath (N), and in the main arm of a Callendar-Griffiths bridge (O). The short tube also in series with a similar and equal standard resistance coil was connected in the compensating arm of the bridge, *i.e.*, the connections as used in platinum thermometry. The current was supplied by a battery of six two-volt accumulators (P), and in the battery circuit were connected sliding-contact wire

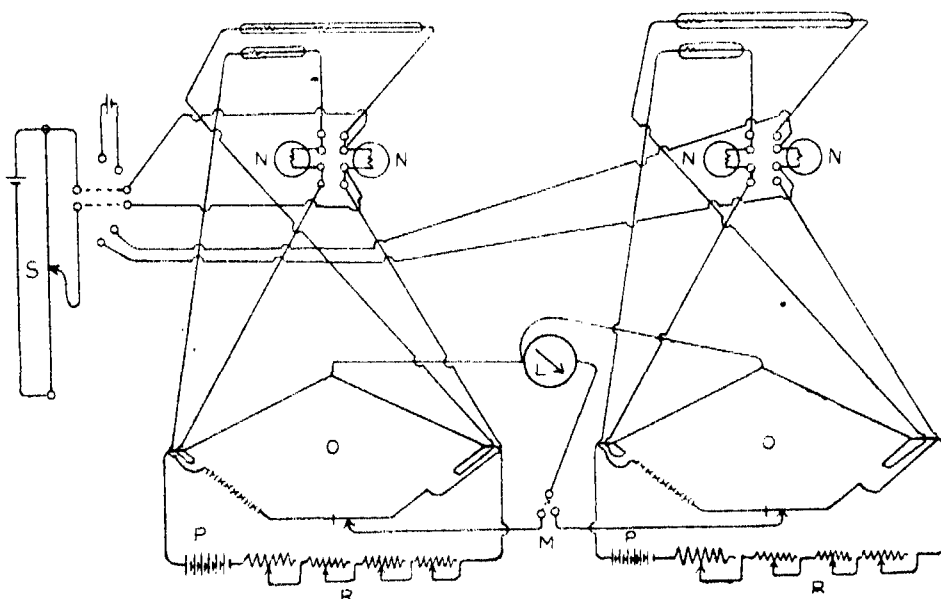


FIG. 9.

rheostats (R), which permitted a very sensitive method of increasing or decreasing the current in the circuit. From the terminals of the standard resistance coil in the main arm of the bridge wires were connected to one circuit of an accurate potentiometer (S) supplied by the Cambridge & Paul Instrument Co. and of the slide type. A motor-driven Gaede molecular pump provided the means of obtaining the necessary variation of pressure in the system of tubes.

#### (8) *Measurement of Current.*

As mentioned above, leading wires were connected from the terminals of a 1-ohm standard resistance coil to one circuit of a slide potentiometer, thus

enabling a direct reading of the strength of the current flowing through the coil, and therefore through the wire in the tubes, to be observed. The scale of the slide-wire was subdivided so that a reading corresponding to 0·0001 volt could be taken, and a Weston normal cell, which had been tested previously and found to be accurate—1·0183 volts—was used in conjunction with the instrument. By this means the measurement of current was made with a probable accuracy of 0·0002 ampere.

(9) *Measurement of Resistance.*

The equation for the total conductive heat loss from the wire may be written

$$\frac{C^2 R}{Jl} = \frac{2\pi K \theta}{\log_e r/r_1},$$

where  $l$  is the effective length of wire and  $R$  the total resistance of this length.

It was considered that it would be more convenient to use in the calculations the value of the resistance per unit length,  $R/l$ , rather than that of the total resistance, and on this account a separate experiment was made to determine the resistance per unit length of the wire actually used in the apparatus. For this purpose two lengths of approximately 1 metre each of the wire were mounted in the form of coils on mica, and the actual resistance of each was measured while immersed in an ice bath and also in steam, using a hypsometer. From the values obtained of the resistance per unit length, using one of the Callendar-Griffiths bridges after having been calibrated previously for the purpose, of the wire at the temperature of ice and of steam, the resistance per unit length at any temperature within the range of the investigation could be calculated with sufficient accuracy.

The results obtained were as follows :—

	1.	2.
Length of wire .....	99·70 cm.	99·65 cm.
Resistance at 0° C. ....	5·2930 ohms	5·2810 ohms.
Temperature of steam .....	100·18° C.	100·18° C.
Resistance at 100·18° C. ....	7·3420 ohms	7·3320 ohms
R/l at 0° C. ....	0·05309 ohm	0·05299 ohm
R/l at 100·18° C. ....	0·07364 ohm	0·07357 ohm
Mean value of R/l at 0° C. ....	0·05304 ohm.	
Mean value of R/l at 100·18° C. ....	0·07361 ohm.	

(10) *Measurement of Temperature.*

The temperature measurements were made by means of the platinum wires in the apparatus, using each pair as a compensated platinum thermometer.

The Callendar-Griffiths bridges used were supplied by the Cambridge Scientific Instrument Company, the coils being of manganin provided with mercury contacts and on the binary scale, *i.e.*, 1,280, 640 . . . 10 cm. of bridge wire. The sliding contact on the bridge wire was fitted with a vernier so that readings of 0.01 cm. could be taken, the resistance of the bridge wire being 0.01 ohm per centimetre approximately. Each bridge was carefully calibrated, the coils being calibrated in terms of the largest.

Using the calibrated values of the coils, etc., the fundamental interval of each pair of wires was next determined by the usual method, using the temperature of melting ice and of steam.

The results, in terms of the bridge wire, were :—

	Narrow.	Wide.
Temperature of bath	0° C.	0° C.
$R_0$ . . . . .	137.800 cm.	137.741 cm.
Temperature of bath	100.107° C.	100.107° C.
$R_{100.107}$ . . . . .	191.300 cm.	191.267 cm.
Fundamental interval	53.500 cm.	53.526 cm.

The close agreement of the above results with the two sets of tubes is evidence of the success attained in the construction of the apparatus.

The fundamental intervals being known, any temperature could be chosen and settings of the bridges calculated so that the wire in each tube would correspond to this temperature when the bridges were balanced by using suitable currents, and in the experimental work it was arranged that this temperature was the same for each pair.

The average temperature coefficient of the manganin coils being taken as 0.00001 and the maximum temperature of the coils during the experiments having been found to be 40° C., the heating effect of the current in the coils would produce a probable error of not more than 0.001° C. in the temperature measurements.

For the correction of platinum temperatures to the air scale, Callendar's equation

$$t - t_{pt} = \delta \cdot t (t - 100) \cdot 10^{-4}$$

was used, the value of  $\delta$  being taken as 1.50. A variation of 1 per cent. in



this value would introduce an error of not more than  $0.003^{\circ}$  C. in the temperature measurements.

It was essential to the success of the experimental work that the temperature of the external surface of the tubes should be kept constant and uniform throughout an experiment. With this object in view, a considerable time was spent in the trial of various types of stirring devices. Finally, it was found that the best method was to use two motor-driven paddle-wheels, three-bladed, 7 cm. in diameter, rotating in a horizontal plane, one situated near the middle of the tank immediately above the main tubes, the other near the end of the tank a little below the level of the main tubes. The mounting of the paddles was such that no vibration of the tank and apparatus was set up. By this means it was found possible to maintain a steady but rapid circulation of the ice and water in the tank, ground ice being added at frequent intervals, and to keep the temperature constant for a considerable period.

#### (11) *Measurement of Pressure.*

The pressure variations to which the gas under investigation was subjected ranged from about 0.001 mm. to 76 cm. of mercury. To measure the pressures, use was made of the mercury manometer down to 0.5 cm., a cathetometer microscope from 0.5 to 0.5 cm., and the McLeod gauge below 0.5 cm.

#### (12) *Experimental Procedure.*

In the first series of experiments, atmospheric air, free from dust and carbon dioxide and dried by means of phosphorus pentoxide, was used in the apparatus. The tubes having been filled with the gas so that the pressure was approximately that of the atmosphere, a convenient temperature was chosen and the settings of the two bridges, such that the wire in each system would correspond to this temperature, were calculated from the fundamental intervals, etc. The bath was then filled with distilled water and crushed ice, the stirring apparatus was set in motion and, after allowing time for the temperature of the bath to become uniform and constant, the electric currents were switched on in the two systems. The currents were then adjusted by means of the rheostats in each system until the bridges were balanced, and allowing the systems to reach a steady state of temperature, which usually occupied about half an hour, the current flowing through each system was measured by the potentiometer. The pressure was then taken from observations of the U-tube manometer in conjunction with the barometric height in the laboratory. Next, the pressure of the gas in the

apparatus was reduced by about 10 cm. of mercury, using the Gaede pump, and where necessary the currents were adjusted by means of the rheostats until the bridges were again balanced, the currents and pressure being again observed. This process was repeated until a series of 15 or 16 readings at different pressures were obtained, the cathetometer microscope being used at the lower pressures and the McLeod gauge for the lowest pressures of all. A series of readings as briefly outlined above occupied a period of about 5 hours. Two further similar series of readings were taken using different settings of the bridges to correspond to two other temperatures of the wires.

### (13) Calculation of Results.

The series of readings obtained in the case of atmospheric air are shown in Tables I to VI, the narrow and wide systems of tubes being indicated on each table.

From the results indicated in these tables, curves were drawn showing the variation of the equivalent conductivity with pressure. One pair of such curves is shown in fig. 10, taken from Tables I and II. Curves were also drawn

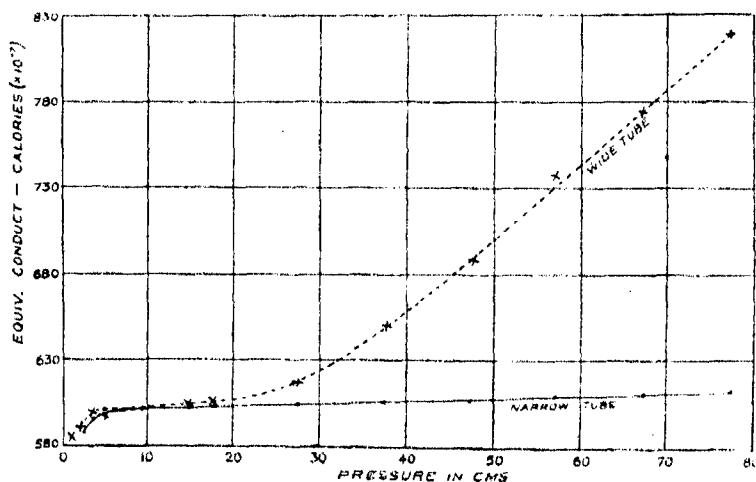


FIG. 10.

plotting the values of the square of the current against the pressure for each pair of tubes. From the two sets of curves, values of the thermal conductivity of the gas for each of the three gradients were obtained in the manner described above. These values are shown at the foot of Tables II, IV and VI, giving also in each case the value of the constant  $\alpha$  (cf. § 4) obtained by this method,

Table I.—Atmospheric Air.

## Narrow Tubes—

Temperature of bath .. .. . 0° C.

,, wire .. .. . 24·105° C.

R/l at 24·105° C. .. .. . 0·058047 ohm.

Radiation at 24·105° C. .. .. . 0·0000126 cal./cm.

$p$ .	$C_N$ .	$W_N$ .	$W_N$ corrected.	$\theta_N$ .	$\theta$ .	$K_N$ .
77·39	0·4052	0·0022778	0·0022652	0·028	24·077	0·0000612
67·06	0·4046	22713	22587	0·028	24·077	610
56·99	0·4040	22643	22517	0·028	24·077	608
46·86	0·4038	22623	22497	0·028	24·077	608
37·23	0·4035	22589	22463	0·028	24·077	607
27·23	0·4032	22554	22428	0·028	24·077	606
17·52	0·4030	22533	22407	0·028	24·077	605
13·03	0·4029	22523	22397	0·028	24·077	605
9·69	0·4026	22489	22363	0·028	24·077	604
8·43	0·4025	22478	22352	0·028	24·077	604
7·27	0·4024	22466	22340	0·028	24·077	603
5·19	0·4020	22420	22294	0·028	24·077	602
3·17	0·4005	22253	22127	0·027	24·078	598
2·15	0·3979	21966	21840	0·027	24·078	590
1·03	0·3941	21548	21422	0·026	24·079	579
0·071	0·2825	11071	10945	0·014	24·091	296

Table II.—Atmospheric Air.

## Wide tubes—

Temperature of bath .. .. . 0° C.

,, wire .. .. . 24·105° C.

R/l at 24·105° C. .. .. . 0·058047 ohm.

Radiation at 24·105° C. .. .. . 0·0000126 cal./cm.

$p$ .	$C_W$ .	$W_W$ .	$W_W$ corrected.	$\theta_W$ .	$\theta$ .	$K_W$ .
77·39	0·4214	0·0024636	0·0024510	0·013	24·092	0·0000613
67·06	0·4122	23572	23446	0·012	24·093	778
56·99	0·4015	22364	22238	0·012	24·093	738
46·86	0·3878	20864	20738	0·011	24·094	688
37·23	0·3768	19698	19572	0·010	24·095	649
27·23	0·3684	18830	18704	0·010	24·095	620
17·52	0·3645	18432	18306	0·010	24·095	607
13·03	0·3636	18341	18215	0·010	24·095	604
9·69	0·3633	18312	18186	0·009	24·096	603
8·43	0·3634	18322	18196	0·009	24·096	604
7·27	0·3633	18312	18186	0·009	24·096	603
5·19	0·3625	18231	18105	0·009	24·096	601
3·17	0·3618	18159	18033	0·009	24·096	598
2·15	0·3613	18110	17984	0·009	24·096	597
1·03	0·3586	17841	17715	0·009	24·096	586
0·071	0·2697	10092	9966	0·005	24·100	330

K at 12·062° C., 0·0000604; Value of  $\alpha$ , 1·2290; Value of  $\alpha$  calc., 1·2289.

Table III.—Atmospheric Air.

Narrow tubes—

Temperature of bath .. .. 0° C.

" wire .. .. 19.484° C.

R/l at 19.484° C. .. .. 0.057087 ohm.

Radiation at 19.484° C. .. .. 0.0000096 cal./cm.

$p$ .	$C_N$ .	$W_N$ .	$W_N$ corrected.	$\theta_N$ .	$\theta$ .	$K_N$ .
76.10	0.3661	0.0018286	0.0018190	0.022	19.462	0.0000609
62.50	0.3655	18227	18136	0.022	19.462	607
55.51	0.3651	18186	18090	0.022	19.462	605
46.68	0.3646	18136	18040	0.022	19.462	604
36.47	0.3643	18107	18011	0.022	19.462	602
26.30	0.3642	18097	18001	0.022	19.462	602
16.14	0.3640	18077	17981	0.022	19.462	601
12.90	0.3640	18077	17981	0.022	19.462	601
10.47	0.3637	18047	17951	0.022	19.462	601
8.61	0.3635	18028	17932	0.022	19.462	600
6.67	0.3632	17998	17902	0.022	19.462	599
4.39	0.3628	17957	17861	0.022	19.462	598
2.57	0.3627	17918	17822	0.022	19.462	596
1.01	0.3565	17340	17244	0.021	19.463	577
0.329	0.3445	16192	16096	0.020	19.464	539
0.069	0.2523	08684	08588	0.011	19.473	287

Table IV.—Atmospheric Air.

Wide tubes—

Temperature of bath .. .. 0° C.

" wire .. .. 19.484° C.

R/l at 19.484° C. .. .. 0.057087 ohm.

Radiation at 19.484° C. .. .. 0.0000096 cal./cm.

$p$ .	$C_W$ .	$W_W$ .	$W_W$ corrected.	$\theta_W$ .	$\theta$ .	$K_W$ .
76.10	0.3734	0.0019023	0.0018927	0.010	19.474	0.0000778
62.50	0.3618	17859	17863	0.009	19.475	730
55.51	0.3552	17213	17117	0.009	19.475	704
46.68	0.3465	16381	16285	0.008	19.476	670
36.47	0.3375	15541	15445	0.008	19.476	635
26.30	0.3316	15001	14905	0.008	19.476	613
16.14	0.3292	14786	14690	0.008	19.476	604
12.90	0.3288	14750	14654	0.008	19.476	602
10.47	0.3284	14714	14618	0.008	19.476	601
8.61	0.3282	14696	14600	0.008	19.476	601
6.67	0.3281	14686	14590	0.008	19.476	600
4.39	0.3277	14652	14556	0.008	19.476	599
2.57	0.3269	14582	14486	0.008	19.476	594
1.01	0.3241	14331	14235	0.007	19.477	583
0.329	0.3154	13572	13476	0.007	19.477	552
0.069	0.2412	07937	07841	0.004	19.480	320

K at 9.479° C., 0.0000600; Value of  $\alpha$ , 1.2291; Value of  $\alpha$  calc., 1.2289.

Table V.—Atmospheric Air.

Narrow tubes—

Temperature of bath .. .. . 0° C.

,, wire .. .. . 14·862° C.

R/l at 14·862° C. .. .. . 0·056127 ohm.

Radiation at 14·862° C. .. .. . 0·0000065 cal./cm.

$p$ .	$C_N$ .	$W_N$ .	$W_N$ corrected.	$\theta_N$ .	$\theta$ .	$K_N$ .
76·10	0·3208	0·0013804	0·0013739	0·017	14·845	0·0000602
65·40	0·3205	13778	13713	0·017	14·845	801
55·65	0·3202	13753	13688	0·017	14·845	800
45·95	0·3201	13744	13679	0·017	14·845	800
35·85	0·3198	13719	13654	0·017	14·845	599
25·50	0·3198	13719	13654	0·017	14·845	599
15·67	0·3195	13694	13629	0·017	14·845	598
11·16	0·3193	13676	13611	0·017	14·845	597
9·01	0·3192	13668	13603	0·017	14·845	596
6·91	0·3189	13642	13577	0·017	14·845	595
4·61	0·3185	13608	13543	0·017	14·845	594
2·25	0·3174	13515	13450	0·017	14·845	590
0·653	0·3109	12965	12900	0·016	14·846	566
0·243	0·2913	11382	11317	0·014	14·848	496
0·093	0·2441	07993	07928	0·010	14·852	348

Table VI.—Atmospheric Air.

Wide tubes—

Temperature of bath .. .. . 0° C.

,, wire .. .. . 14·862° C.

R/l at 14·862° C. .. .. . 0·056127 ohm.

Radiation at 14·862° C. .. .. . 0·0000065 cal./cm.

$p$ .	$C_W$ .	$W_W$ .	$W_W$ corrected.	$\theta_W$ .	$\theta$ .	$K_W$ .
76·10	0·3226	0·0013961	0·0013896	0·007	14·855	0·0000748
65·40	0·3148	13293	13228	0·007	14·855	712
55·65	0·3073	12668	12603	0·007	14·855	679
45·95	0·2986	11961	11896	0·006	14·856	641
35·85	0·2927	11492	11427	0·006	14·856	613
25·50	0·2896	11251	11186	0·006	14·856	602
15·67	0·2883	11150	11085	0·006	14·856	597
11·16	0·2881	11133	11068	0·006	14·856	596
9·01	0·2881	11133	11068	0·006	14·856	596
6·91	0·2881	11133	11068	0·006	14·856	596
4·61	0·2877	11104	11039	0·006	14·856	594
2·25	0·2869	11042	10977	0·006	14·856	591
0·653	0·2819	10659	10594	0·006	14·856	570
0·243	0·2687	09685	09620	0·005	14·857	518
0·093	0·2314	07182	07117	0·004	14·858	383

K at 7·437° C., 0·0000596; Value of  $\alpha$ , 1·2292; Value of  $\alpha$  calc., 1·2289.

together with the value obtained by calculation from the dimensions of the apparatus.

With reference to fig. 10, it should be observed that the zero of the conductivity scale on the left is about 13·5 cm. below the pressure scale at the base of the figure. The observations are plotted on a large scale to show the characteristic difference due to the greater loss by convection in the wide tubes represented by the dotted curve, as compared with the narrow tubes represented by the full curve. It is evident that such losses, taken in conjunction with the temperature drop in the glass wall and with other corrections which have hitherto been neglected, are quite competent to explain the remarkable differences between the results of previous observers.

(14) *Variation of Conductivity with Temperature.*

In the deduction of the thermal conductivity at 0° C., the manner in which all previous experimenters have expressed their results, it may be pointed out that the results in several cases have been reduced by interpolation assuming some coefficient from experiments in which the gradients have been as much as 90° C. It is obvious that results so obtained cannot be of much value. In the case of the experiments of Hercus and Laby and of Todd, the experimental scheme was such that only one gradient was possible and this so large, 90° C. in the case of Todd and 20° C. in the case of Hercus and Laby, that the observations corresponded to a value of  $K$  at a mean temperature of 55° C. and 22° C. respectively, and were reduced to  $K$  at 0° C. by assuming some predetermined value of a coefficient of variation with temperature. The results on these two cases for  $K$  at 0° C. were 0·0000495 and 0·0000540, a variation of about 10 per cent.

Assuming that the law of variation of thermal conductivity with temperature may be written

$$K_{\theta} = K_0 (1 + \gamma \cdot \theta)$$

it is found that for atmospheric air

$$\gamma = 0\cdot000297$$

and that

$$K_0 = 0\cdot0000583.$$

(15) *Accuracy of the Method.*

The maximum error in  $K$ , expressed as a percentage, can be readily estimated in terms of the accuracy involved in the measurement of the quantities  $C$ ,  $R/l$ ,  $\theta$ ,  $r_1$ ,  $r_2$ , etc. Assuming an error of 0·0001 amp. in the measurement

of C, 0.0001 ohm in R, 0.01 cm. in the setting of the bridges, etc., the percentage error in K for the lowest gradient taken in the case of atmospheric air has been calculated to be 0.33 per cent., and for the highest gradient 0.27 per cent.

(16) *Conductivity of Hydrogen.*

In the second series of experiments hydrogen was used.

The gas was prepared in a pure state by the electrolysis of pure barium hydroxide in solution, a voltameter of large capacity having been specially constructed for the purpose. This voltameter was connected directly to the drying chamber so that the gas was thoroughly dried before passing into the tubes, the whole apparatus having been first completely exhausted by means of the pumps and the charcoal pockets immersed in liquid air. The experimental procedure adopted was exactly the same as in the experiments on atmospheric air and three sets of observations with the wire at three different temperatures were taken. Owing, however, to the much greater transmission of heat through the gas and the consequent necessity of using larger currents in the electrical circuits than in the case of air, it was found necessary to employ smaller gradients of temperature across the gas.

The results obtained are shown in Tables VII to XII, which are arranged exactly as in the case of air, fig. 11 shows the curves obtained by plotting the values of the equivalent conductivities against the pressure taken from Tables XI and XII.

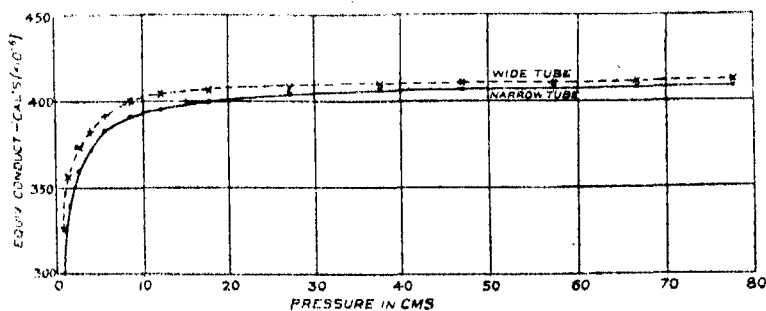


FIG. 11.

It will be observed that the temperature drop across the wall of the tube, due to the greater transmission of heat, is greater in comparison with the gradient across the gas than in the case of the results for air, giving rise to a difference of about 0.5 per cent. in the gradients for the narrow and wide

Table VII.—Hydrogen.

Narrow tubes—

Temperature of bath .. .. . 0° C.

,, wire .. .. . 8.393° C.

R/l at 8.393° C. .. .. . 0.054783 ohm.

Radiation at 8.393° C. .. .. . 0.0000022 cal./cm.

<i>p.</i>	<i>C<sub>N</sub></i>	<i>W<sub>N</sub></i>	<i>W<sub>N</sub> corrected.</i>	<i>θ<sub>N</sub></i>	<i>θ.</i>	<i>K<sub>N</sub></i>
75.84	0.6340	0.0052630	0.0052608	0.065	8.328	0.0004111
66.34	0.6338	52595	52573	0.065	8.328	4108
56.74	0.6336	52563	52541	0.065	8.328	4105
46.34	0.6334	52529	52507	0.064	8.329	4102
39.74	0.6331	52479	52457	0.064	8.329	4098
31.04	0.6325	52380	52358	0.064	8.329	4091
21.52	0.6310	52132	52110	0.064	8.329	4071
16.62	0.6296	51900	51878	0.064	8.329	4053
12.02	0.6285	51722	51700	0.063	8.330	4039
7.08	0.6229	50800	50778	0.062	8.331	3966
5.12	0.6183	50055	50033	0.061	8.332	3908
3.86	0.6122	49072	49050	0.060	8.333	3830
2.90	0.6059	48048	48026	0.059	8.334	3750
1.78	0.5925	45944	45922	0.056	8.337	3585
0.88	0.5676	42183	42161	0.052	8.341	3289
0.10	0.4737	29379	29357	0.036	8.357	2286

Table VIII.—Hydrogen.

Wide tubes—

Temperature of bath .. .. . 0° C.

,, wire .. .. . 8.393° C.

R/l at 8.393° C. .. .. . 0.054873 ohm.

Radiation at 8.393° C. .. .. . 0.0000022 cal./cm.

<i>p.</i>	<i>C<sub>w</sub></i>	<i>W<sub>w</sub></i>	<i>W<sub>w</sub> corrected.</i>	<i>θ<sub>w</sub></i>	<i>θ.</i>	<i>K<sub>w</sub></i>
75.84	0.5751	0.0043306	0.0043284	0.022	8.371	0.0004135
66.34	0.5747	43244	43222	0.022	8.371	4129
56.74	0.5745	43215	43193	0.022	8.371	4127
46.34	0.5743	43185	43163	0.022	8.371	4124
39.74	0.5740	43140	43118	0.022	8.371	4119
31.04	0.5732	43019	42997	0.022	8.371	4108
21.52	0.5716	42779	42757	0.022	8.371	4085
16.62	0.5703	42584	42562	0.022	8.371	4066
12.02	0.5691	42406	42384	0.022	8.371	4049
7.08	0.5648	41770	41748	0.022	8.371	3989
5.12	0.5614	41266	41244	0.021	8.372	3940
3.86	0.5574	40680	40658	0.021	8.372	3884
2.90	0.5525	39968	39946	0.021	8.372	3816
1.78	0.5430	38605	38583	0.020	8.373	3685
0.88	0.5231	35827	35805	0.019	8.374	3420
0.10	0.4466	26115	26093	0.013	8.380	2490

**K** at 4.218° C., 0.0004088; Value of  $\alpha$ , 1.2245; Value of  $\alpha$  calc., 1.2289.



Table IX.—Hydrogen.

Narrow tubes—

Temperature of bath .. .. 0° C.

,, wire .. .. 6.545° C.

R/l at 6.545° C. .. .. 0.054399 ohm.

Radiation at 6.545° C. .. .. 0.0000018 cal./cm.

<i>p.</i>	<i>C<sub>N</sub></i>	<i>W<sub>N</sub></i>	<i>W<sub>N</sub></i> corrected.	<i>θ<sub>N</sub></i>	<i>θ.</i>	<i>K<sub>N</sub></i>
76.56	0.5602	0.0040802	0.0040784	0.050	6.495	0.0004086
66.01	0.5601	40788	40770	0.050	6.495	4085
55.31	0.5602	40802	40784	0.050	6.495	4086
45.91	0.5600	40773	40755	0.050	6.495	4083
36.81	0.5598	40745	40727	0.050	6.495	4081
26.16	0.5590	40626	40608	0.050	6.495	4069
18.41	0.5577	40440	40422	0.050	6.495	4050
11.55	0.5570	40338	40320	0.049	6.496	4039
8.83	0.5556	40134	40116	0.049	6.496	4019
5.05	0.5493	39229	39211	0.048	6.497	3927
3.15	0.5421	38207	38189	0.047	6.498	3824
2.21	0.5332	36963	36945	0.045	6.500	3699
1.13	0.5103	33854	33836	0.042	6.503	3386
0.71	0.4875	30899	30881	0.038	6.507	3089
0.33	0.4390	25055	25037	0.031	6.514	2501

Table X.—Hydrogen.

Wide tubes—

Temperature of bath .. .. 0° C.

,, wire .. .. 6.545° C.

R/l at 6.545° C. .. .. 0.054399 ohm.

Radiation at 6.545° C. .. .. 0.0000018 cal./cm.

<i>p.</i>	<i>C<sub>w</sub></i>	<i>W<sub>w</sub></i>	<i>W<sub>w</sub></i> corrected.	<i>θ<sub>w</sub></i>	<i>θ.</i>	<i>K<sub>w</sub></i>
76.56	0.5071	0.0033435	0.0033417	0.017	6.528	0.0004094
66.01	0.5070	33421	33403	0.017	6.528	4092
55.31	0.5069	33407	33389	0.017	6.528	4091
45.91	0.5068	33394	33376	0.017	6.528	4089
36.81	0.5068	33368	33350	0.017	6.528	4086
26.16	0.5060	33288	33270	0.017	6.528	4076
18.41	0.5046	33104	33086	0.017	6.528	4053
11.55	0.5036	32974	32956	0.017	6.528	4038
8.83	0.5022	32790	32772	0.017	6.528	4015
5.05	0.4971	32129	32111	0.017	6.528	3984
3.15	0.4915	31407	31389	0.016	6.529	3845
2.21	0.4844	30508	30490	0.016	6.529	3735
1.13	0.4676	26428	26410	0.015	6.530	3480
0.71	0.4498	26306	26288	0.014	6.531	3219
0.33	0.4094	21793	21775	0.011	6.534	2665

K at 3.289° C., 0.0004079; Value of  $\alpha$ , 1.2241; Value of  $\alpha$  calc., 1.2289.

Table XI.—Hydrogen.

Narrow tubes—

Temperature of bath .. .. . 0° C.

" wire .. .. . 4.686° C.

R/l at 4.686° C. .. .. . 0.054015 ohm.

Radiation at 4.686° C. .. .. . 0.0000012 cal./cm.

<i>p.</i>	<i>C<sub>N</sub>.</i>	<i>W<sub>N</sub>.</i>	<i>W<sub>N</sub> corrected.</i>	<i>θ<sub>N</sub>.</i>	<i>θ.</i>	<i>K<sub>N</sub>.</i>
77.37	0.4755	0.0029188	0.0029176	0.036	4.650	0.0004083
66.92	0.4757	29213	29201	0.036	4.650	4086
57.85	0.4758	29224	29212	0.036	4.650	4088
47.13	0.4752	29150	29138	0.036	4.650	4078
37.24	0.4748	29102	29090	0.036	4.650	4071
27.53	0.4740	29005	28993	0.036	4.650	4058
17.80	0.4709	22825	22813	0.035	4.651	4003
12.13	0.4687	29361	28349	0.035	4.651	3966
8.71	0.4663	28071	28059	0.034	4.652	3926
5.97	0.4624	27602	27590	0.034	4.652	3859
3.97	0.4553	26762	26750	0.033	4.653	3741
2.27	0.4475	25854	25842	0.032	4.654	3613
1.29	0.4350	24428	24416	0.030	4.656	3412
0.59	0.4087	21567	21555	0.027	4.659	3011
0.23	0.3663	17322	17310	0.021	4.665	2415

Table XII.—Hydrogen.

Wide tubes—

Temperature of bath .. .. . 0° C.

" wire .. .. . 4.686° C.

R/l at 4.686° C. .. .. . 0.054015 ohm.

Radiation at 4.686° C. .. .. . 0.0000012 cal./cm.

<i>p.</i>	<i>C<sub>w</sub>.</i>	<i>W<sub>w</sub>.</i>	<i>W<sub>w</sub> corrected.</i>	<i>θ<sub>w</sub>.</i>	<i>θ.</i>	<i>K<sub>w</sub>.</i>
77.37	0.4315	0.0024037	0.0024025	0.012	4.674	0.0004111
66.92	0.4316	24048	24036	0.012	4.674	4113
57.85	0.4318	24070	24058	0.012	4.674	4116
47.13	0.4305	23925	23913	0.012	4.674	4092
37.24	0.4298	23849	23837	0.012	4.674	4079
27.53	0.4291	23770	23758	0.012	4.674	4065
17.80	0.4288	23738	23726	0.012	4.674	4060
12.13	0.4275	23593	23581	0.012	4.674	4035
8.71	0.4256	23385	23373	0.012	4.674	3999
5.97	0.4225	23044	23032	0.012	4.674	3941
3.97	0.4176	22515	22503	0.012	4.674	3851
2.27	0.4123	21945	21933	0.011	4.675	3752
1.29	0.4011	20769	20757	0.011	4.675	3550
0.59	0.3822	18857	18845	0.010	4.676	3223
0.23	0.3471	15554	15542	0.008	4.678	2657

K at 2.355° C., 0.0004068; Value of  $\alpha$ , 1.2243; Value of  $\alpha$  calc., 1.2289.

tube systems. This is brought out in the values of the equivalent conductivities obtained from the two systems and also in the values of the constant  $\alpha$  obtained from the three sets of observations.

Using the law,  $K_p = K_0 (1 + \gamma \cdot p)$ , as in the case of air, it is found that for hydrogen

$$\gamma = 0.00265$$

and that

$$K_0 = 0.0004043.$$

This compares with a mean value of 0.0004026 obtained from the results of four previous observers using the hot-wire method, and is from 5 to 25 per cent. greater than previous results published. Some justification that the higher result is the more accurate is afforded by reference to fig. 11 in which the apparent conductivity of hydrogen is plotted against the pressure. For hydrogen the convective losses of heat are small even at atmospheric pressure, but on the other hand the critical pressure at which the molecular mean free path becomes comparable with the thickness of the gas layer is much higher than in the case of air. In the present method, the pressure at which the convective losses become vanishingly small can be accurately estimated and the practice used by previous observers of indiscriminately lowering the pressure to obviate these losses is therefore dangerous if carried to the point where the conductivity has begun to vary with the pressure, due to the reason considered above.

The work described above has been carried out in the Physics Department of the Royal College of Science, the preliminary experiments commencing in 1920 and the final work completed in July, 1923. The authors take this opportunity to express their thanks to Prof. H. L. Callendar for his permission to carry out the work, and their appreciation of his very helpful criticism during the course of the work; also to Mr. W. J. Colebrook, whose skilful direction of the mechanical work contributed largely to the success of the experiments.

The work is being continued with respect to other gases and with a view to investigating the question of the variation of thermal conduction through gases over wider ranges of temperature.

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*The Structure of Molecules in Relation to their Optical Anisotropy.—Part II—Benzene and Cyclohexane.*

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1. *Introduction.*

In Part I\* the view was advanced that the optical anisotropy of the molecules of a gas which is evidenced by the depolarisation of the light scattered by it can to a large extent be attributed to the mutual influence of the doublets induced in the different atoms of the molecule by the electrical field of the incident radiation.

Assuming that each atom is isotropic, and assuming the refractivity and anisotropy of the molecules of hydrogen, oxygen and nitrogen, the atomic refractivity and the distance apart between the "optical centres" was calculated in these cases. Extending the treatment to the case of triatomic molecules with the three atoms in a straight line, and using the previously obtained values for the atomic refractivities of nitrogen and oxygen and the diamond value of the atomic refractivity of carbon, the optical anisotropies of the gases  $N_2O$ ,  $CO_2$  and  $CS_2$  were calculated. The corresponding values of the depolarisation of the transversely scattered light were found to be in fair agreement with experiment. In this paper the work is extended to the two organic molecules, benzene and cyclohexane.

2. *Polarisation of the Scattered Light in Benzene and Cyclohexane.*

The imperfection of polarisation of the transversely scattered light in benzene vapour has been recently measured by Raman and Rao† and by Ganesan.‡ Their values are 0.068 and 0.066 respectively. We shall adopt the average of these two values, 0.067. Ganesan has also made measurements on a few benzene derivatives with the following results :—

Toluene .....	0.064
<i>m</i> -Xylene .....	0.067
Chloro-Benzene .....	0.078
Bromo-benzene .....	0.078

\* 'Roy. Soc. Proc.,' A, vol. 107, p. 684.

† 'Phil. Mag.,' vol. 46, p. 426 (1923).

‡ 'Phil. Mag.,' vol. 49, p. 1216 (1925).

It is significant that the values do not differ much from each other, which shows that the major part of the anisotropy has its origin in the benzene structure.

No previous measurements on the depolarisation of the light scattered by cyclohexane vapour have been recorded. The author has recently measured its value, using sunlight for illumination, and found it to be 0.011. A simple glass apparatus was employed for the measurement, and as the apparatus has been found particularly convenient for work with vapours which require heating, and as only small quantities of the substances are required, it may be worth while to describe it briefly.

Two bulbs, A and B, were blown on a tube of clear glass of about 2 cm. internal diameter, particular care being taken to see that there were no streaks or uneven portions on the bottom of the bulb B. The purpose of the second bulb is to prevent light diffused from places on the walls of the first bulb A which are struck by the incident light from reaching the observing window. The stem of the tube was about 20 cm. in length, and its end was drawn out into a horn (fig. 1). After cleaning and drying, a small quantity of the pure

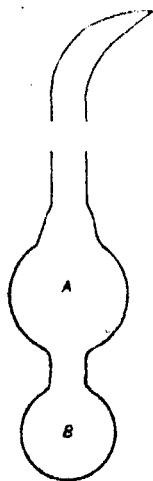


FIG. 1.

liquid was introduced into the bulb, and after evacuation with a pump, the tube was sealed off. The bulb was painted over with black paint, except for two windows in A for the entry and exit of a narrow pencil of sunlight and a small rectangular window in the bottom of B for observation. The tube was mounted horizontally inside a big iron cross-tube blackened inside and provided with suitable diaphragms to shut out stray light, and the measurements of the depolarisation were made visually with a double image prism and nicol. Arrangements were made to heat up the tube to different temperatures by means of an electric current. When the measurements are made with a view to obtain the optical anisotropy of the molecule, it is important to keep the density of the vapour as low as possible. The temperature was usually kept below the boiling point of the liquid. Check measurements on the vapours of benzene and carbon disulphide gave values 0.066 and 0.143 against Ganesan's values 0.066 and 0.167.

### 3. Calculation of the Optical Anisotropy of Benzene.

If A, B, C be the polarisations induced in a molecule when its three principal directions are respectively along the direction of an electric field of unit intensity

and of the frequency of the incident radiation, then the ratio of the weak component to the strong in the light scattered perpendicular to the incident beam is\*

$$r = \frac{2(A^2 + B^2 + C^2) - 2(AB + BC + CA)}{4(A^2 + B^2 + C^2) + AB + BC + CA} \quad (1)$$

In the particular case when  $A = B$ , this becomes

$$r = \frac{2(A - C)^2}{9A^2 + 4C^2 + 2AC}.$$

In order to calculate the values of  $A$ ,  $B$  and  $C$  for any molecule, it is necessary to assume some structure for it. In the case of benzene, chemical evidence requires that the six carbon atoms and the six hydrogen atoms are similar. From the further negative evidence that no optically-active derivative of benzene containing a single nucleus has been isolated, it has been held that the six carbon atoms lie in the same plane at the angular points of a regular hexagon,† and that the hydrogen atoms lie in the same plane at the six corners. On the other hand, if we proceed from the analogy of the crystal structures of naphthalene and anthracene as analysed by Sir W. H. Bragg,‡ the carbon atoms would be arranged in a puckered hexagonal ring as in diamond, the hydrogen atoms being joined to the carbons at the tetrahedral angle.

In order to decide which of these structures to adopt, a preliminary calculation was made in which the hydrogen atoms were ignored. The anisotropy of a structure consisting of six carbon atoms was calculated both when they are arranged in a plane ring as in graphite, and when they are arranged in a puckered ring as in diamond. In the former case, the distance between the centres of two neighbouring carbon atoms was assumed to be 1.45 A.U. and in the latter case 1.50 A.U. Calculations were made for two values of the atomic refractivity, viz., (1) the refractivity of carbon in diamond and (2) the refractivity usually ascribed to carbon in organic compounds.

The three principal directions in the molecule were taken to be (1) OX, parallel to 1-3 in fig. 2; (2) OY, perpendicular to 1-3 in the plane of the paper; and (3) OZ, perpendicular both to 1-3 and to the plane of the paper. In the case of the puckered ring structure, the atom-centres 1, 3, 5 lie in the plane of the paper, while 2, 4, 6 lie 0.5 A.U. above this plane.

\* Lord Rayleigh, 'Phil. Mag.', vol. 35, p. 373 (1918).

† J. F. Thorpe, 'Chemistry in the Twentieth Century.'

‡ W. H. Bragg and W. L. Bragg, 'X-rays and Crystal Structure,' chap. XIV.

1. *Plane Ring of Six Carbon Atoms.*—When the field is parallel to the X-axis, the resultant electric intensity at each atom will be confined to the XY plane. The X-components of the polarisations of 1, 3, 4 and 6 will, by symmetry, be the same (fig. 3), say  $ex_1$ , and those of the atoms 2 and 5 will

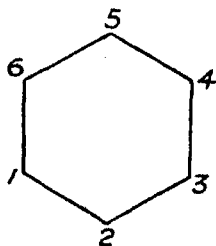


FIG. 2.

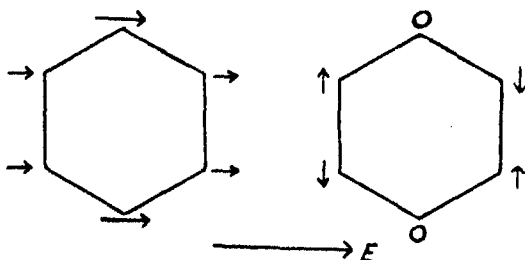


FIG. 3.

also be the same but have a different value, say  $ex_2$ . The  $y$  components of 2 and 5 will vanish, while those at 1, 3, 4 and 6 will be equal to each other, but alternate in sign.

The  $x$ -component of the electric intensity at any atom will be given by

$$E' = E + \Sigma \frac{3a^2 - r^2}{r^5} ex_n + \Sigma \frac{3ab}{r^5} . ey_n + \Sigma \frac{3ac}{r^5} ez_n, \quad (2)$$

where  $E$  is the electric vector in the incident light  $ex_n, ey_n, ez_n$  are the components of the polarisation of any other atom in the molecule whose co-ordinates with respect to the atom we are considering are  $a, b, c$ , and  $r$  is the distance between the two atoms. The summation is extended to all the other atoms in the molecule.

The polarisation due to this field is given by

$$ex = e^2 \lambda E'$$

where  $e^2 \lambda$  is obtained from Lorentz's equation for the atomic refractivity

$$\frac{A}{\rho} \frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N_0 e^2 \lambda.$$

$A$  is the atomic weight of the element,  $\rho$  is its density,  $n$  its refractive index, and  $N_0$  the number of molecules in a gram-molecule.

Taking the atomic refractivity of diamond to be  $2.124$ ,\* we get the value of  $e^2 \lambda$  for carbon to be  $0.836 \times 10^{-24}$ , and calculating the field due to the other atoms, and summing them up with their proper signs, we obtain

\* Part I.

$$1.196 ex_1 = E \times 10^{-24} - 0.151 ex_1 + 0.394 ex_2 - 0.0533 ey_1$$

$$1.196 ex_2 = E \times 10^{-24} + 0.788 ex_1 - 0.041 ex_2 - 0.688 ey_1$$

$$1.196 ey_1 = 0.053 ex_1 - 0.344 ex_2 - 0.603 ey_1.$$

Solving, we get

$$ex_1 = 1.25 E \times 10^{-24}$$

$$ex_2 = 1.77 E \times 10^{-24}$$

$$ey_1 = -0.30 E \times 10^{-24}.$$

The total polarisation parallel to the inducing field is  $4ex_1 + 2ex_2$ , which is equal to  $8.54 E \times 10^{-24}$ .

When the field is parallel to OY, the same value of the polarisation is obtained. The molecule is thus isotropic in the XY plane.

When the field is parallel to OZ, the fields at any atom due to the other atoms oppose each other, thus producing a weaker resultant field and hence a smaller polarisation. Calculating as before, the induced moment of each atom in this case comes out to be  $0.495 E \times 10^{-24}$ , and hence the total for the six atoms is  $2.97 E \times 10^{-24}$ .

The optical anisotropy is thus  $A : B : C = 8.54 : 8.54 : 2.97 = 2.94 : 2.94 : 1$ , and the imperfection of polarisation of the transversely scattered light calculated according to (1) is 0.083.

If the refractivity of carbon is assumed to be that usually adopted in tables of refractivities, namely, 2.44 (for the F line), the polarisations parallel to the field when the field is along the X and Z axes respectively are found to be

$$\left. \begin{aligned} ex_1 &= 1.58 E \times 10^{-24} \\ ex_2 &= 2.34 E \times 10^{-24} \end{aligned} \right\}$$

and

$$ez_1 = 0.534 E \times 10^{-24}$$

leading to a value of the anisotropy  $3.4 : 3.4 : 1$  and a depolarisation of the transversely scattered light of 0.10.

II. *Puckered Ring of Six Carbon Atoms.*—Assumed distance between the centres of two neighbouring carbon atoms = 1.50 A.U. Assumed atomic refractivity of carbon = 2.124.

Starting from the atom on the left-hand bottom corner, the co-ordinates of the centres of the different atoms are given below (see Table I).



TABLE 1.

	<i>a.</i>	<i>b.</i>	<i>c.</i>
1	0	0	0
2	1.225	-0.707	0.500
3	2.450	0	0
4	2.450	1.414	0.500
5	1.225	2.121	0
6	0	1.414	0.500

When the electric vector in the incident light is parallel to the X-axis, the directions of the X- and Y-components of polarisation will be as in figure 3, but

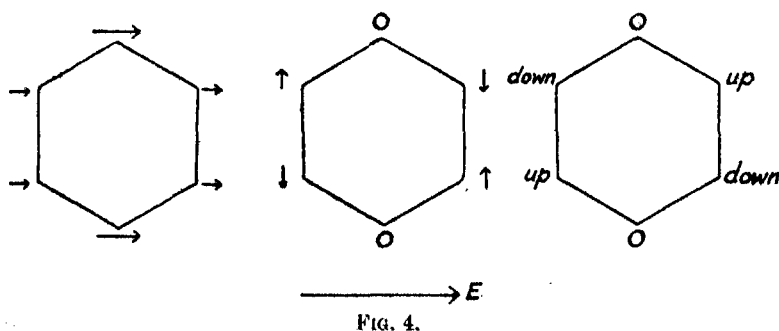


FIG. 4.

since the atoms are not confined to the XY-plane, the Z-components will not vanish. They will be as shown in fig. 4. We have therefore four unknowns to determine, namely,  $ex_1$ ,  $ex_2$ ,  $ey_1$  and  $ez_1$ . The appropriate equations are found to be

$$1.196 ex_1 = E \times 10^{-24} - 0.110 ez_1 + 0.279ex_2 + 0.053ey_1 + 0.018ez_1$$

$$1.196ex_2 = E \times 10^{-24} + 0.559ex_1 - 0.042ex_2 - 0.507ey_1 + 0.484ez_1$$

$$1.196ey_1 = 0.053ex_1 - 0.254ex_2 - 0.438ey_1 - 0.269ez_1$$

$$1.196ez_1 = 0.019ex_1 + 0.242ex_2 - 0.268ey_1 + 0.227ez_1$$

which when solved give

$$ex_1 = 1.11 E \times 10^{-24}$$

$$ex_2 = 1.63 E \times 10^{-24}$$

$$ey_1 = -0.301 E \times 10^{-24}$$

$$ez_1 = 0.512 E \times 10^{-24}$$

The resultant polarisation is along the direction of the field and is given by  $4ex_1 + 2ex_2 = 7.70 E \times 10^{-24}$ .

Writing down the appropriate equations when the incident field is parallel to the Z-axis and solving, we get for the total polarization parallel to the Z-axis  $3.68 E \times 10^{-24}$ . The resultant polarizations in other directions vanish.

The calculated value of  $r$  is 0.050.

If we take the atomic refractivity of carbon to be 2.44, we get  $A : B : C = 10.0 : 10.0 : 4.14$  and  $r = 0.065$ .

III. *Puckered Ring of Six Carbon Atoms with the Hydrogens introduced.*—In the calculations made above, we have altogether ignored the effect of the hydrogen atoms. Their introduction either in the plane of the carbon atoms in Case I or in the appropriate positions in the approximate plane of the puckered ring in Case II can only lead to an increase in the anisotropy. We have already found that if we adopt the plane ring structure, the calculated value of the anisotropy is too high even with the smaller value of the atomic refractivity. Unless therefore we assume that the distance between the optical centres is greater than 1.45 A.U., or that the atoms themselves are distinctly anisotropic with their axis of larger polarization perpendicular to the plane of the ring, we cannot explain the observed anisotropy of benzene with this structure. Since, however, the carbons are bounded on the outside by the hydrogens, it is unlikely that the distance between the optical centres of the carbons is really much greater than the X-ray distances. As for the second alternative, although it is quite likely that in a graphite structure, the atoms are more polarizable perpendicular to the plane than parallel to the plane, since we have nothing definite to go by, it is better for the present not to bring in an unknown factor in the shape of the anisotropy of the individual carbon atom. We shall therefore in what follows adopt the puckered ring structure of the carbon and work out the effect of introducing the hydrogens.

The question of the position of the hydrogen atoms is a difficult one. We shall assume that each hydrogen is joined to its carbon at the tetrahedral angle, the projection of the whole structure upon the average plane of the ring being the familiar graphic formula for benzene. In order to calculate the distance of a hydrogen atom from the centre of a neighbouring carbon atom, we cannot adopt the usual X-ray "diameter" of hydrogen, as in this case the hydrogen is not bounded by other atoms on the outside. In Part I, it was calculated that the distance between the optical centres in a hydrogen molecule is 1.37 A.U. Adding half this distance to the "radius" of a carbon atom, we obtain 1.43 A.U. to be the required distance. The atomic refractivity of hydrogen is assumed to be that calculated in Part I and the refractivity of carbon to be that of diamond.

The calculations were made exactly on the same lines as before, but since we have now to deal with the polarizations of twice as many atoms, we have twice as many unknowns. The appropriate equations for the polarizations of the different atoms were written down, and their solution was obtained by a method of successive approximations. Assuming the values of the polarization of the carbon atoms obtained above when the hydrogens were not present, the polarizations of the hydrogens were calculated neglecting the small influence of the other hydrogen atoms. These were substituted in the equations for the polarization of the carbon atoms, and their solution gave a better approximation to the true values. The operation was repeated a few times until further approximations did not cause any appreciable alteration in the values.

When the field is parallel to the X-axis, the following values were obtained for the polarizations parallel to the field.

$$ex_1 = 1.53 \text{ Ex } 10^{-24}$$

$$ex_2 = 1.98 \text{ Ex } 10^{-24}$$

$$ex_1' = 0.64 \text{ Ex } 10^{-24}$$

$$ex_2' = 0.11 \text{ Ex } 10^{-24}$$

where  $ex_1', ex_2'$  refer to the hydrogen atoms. The resultant polarization parallel to the X-axis is  $4(ex_1 + ex_1') + 2(ex_2 + ex_2')$ , i.e.,  $12.86 \text{ E} \times 10^{-24}$ .

With the field parallel to the Z-axis, the polarizations of the carbon and hydrogen atoms parallel to the field were

$$ez_1 = 0.52 \text{ E} \times 10^{-24}$$

$$ez_1' = 0.29_5 \text{ E} \times 10^{-24}$$

and thus we get for the resultant polarization  $6(ez_1 + ez')$  the value  $4.88 \text{ E} \times 10^{-24}$ .

The polarization when the field is parallel to the Y-axis would be the same as when it is parallel to the X-axis.

The calculated value of the depolarization of the transversely scattered light is 0.074, which may be compared with the experimental value 0.067.

#### 4. The Molecular Refractivity of Benzene.

The mean polarization per unit field averaged over all orientations is  $(A + B + C)/3$ . With the values obtained in the last section, its value is  $10.2 \times 10^{-24}$ . Calculating the molecular refractivity by means of the formula

$$\frac{M}{\rho} \frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N_0 \frac{A + B + C}{3},$$

we find its value to be 25.9 (for the F line). The experimental value of the

molecular refractivity of benzene\* is 26·2 for the D line and 26·7 for the F line. The difference is not large considering the nature of the assumptions involved in the calculations. It may be recalled that the atomic refractivities of carbon and hydrogen which we have used are not the refractivities deduced from the molecular refractivities of organic compounds by the rule of additivity. Such values are likely to be invariably higher owing to the influence of the other atoms in the molecule. If we adopt a plane structure, both the refractivity and the anisotropy are found to be too high.

### 5. *Optical Anisotropy and Refractivity of Cyclohexane (C<sub>6</sub>H<sub>12</sub>).*

Compared with benzene, cyclohexane has a small anisotropy; while the depolarization of the transversely scattered light in the former is 0·067, that in the latter is only 0·011. The extra hydrogen atoms should therefore occupy such positions as will reduce the anisotropy. If we retain the idea that the binding of one carbon atom to another and of a hydrogen to a carbon take place at the tetrahedral angle, the structure of cyclohexane can be derived from that of benzene by adding a hydrogen to each carbon atom, the extra hydrogens being alternately below and above the plane of the paper in fig. 2. The new hydrogens attached to carbon atoms 1, 3 and 5 will be vertically below the plane of the paper, while those attached to 2, 4 and 6 will be vertically above the plane. We assume that the distance of the optical centres of these hydrogen atoms from the centres of the neighbouring carbon atoms to be the same as before, namely 1·43 A.U. We can now calculate the optical anisotropy of such a structure. When the field is parallel to the X- or Y-axis, the polarization of the extra hydrogens (which we shall denote by  $ex_1''$ ,  $ex_2''$ , etc.) will cause a field at the carbons tending to reduce their polarization, and the polarization of the carbons will similarly tend to reduce the field at the hydrogens while when the field is parallel to the Z-axis, the polarizations will help each other. Using the same method of successive approximations, and neglecting the mutual influence of the previous set of hydrogen atoms on the new set, the following values are obtained for the polarisations parallel to the field :—

$$ex_1 = 1·47 \quad E \times 10^{-24}$$

$$ex_2 = 1·90 \quad E \times 10^{-24}$$

$$ex_1' = 0·63 \quad E \times 10^{-24}$$

$$ex_2' = 0·12 \quad E \times 10^{-24}$$

$$ex_1'' = 0·15 \quad E \times 10^{-24}$$

$$ex_2'' = 0·09 \quad E \times 10^{-24}$$

\* 'Landolt Bornstein Tabellen,' p. 977.

Therefore, total polarization parallel to the X-axis =  $13.2 E \times 10^{-24}$ ,  
and

$$ez_1 = 0.86 E \times 10^{-24}$$

$$ez_1' = 0.21 E \times 10^{-24}$$

$$ez_1'' = 0.63 E \times 10^{-24}$$

Therefore, total polarization parallel to the Z-axis =  $10.2 E \times 10^{-24}$ .

From the similarity to the case of benzene, the polarization parallel to the Y-axis will be the same as that parallel to the X-axis, and hence the value of the anisotropy is  $13.2 : 13.2 : 10.2$ . The calculated value of  $r$  is 0.008.

The average polarization obtained from the above data is  $12.2 E \times 10^{-24}$  and the calculated molecular refractivity 31.0, while the observed refractivity is 29.7 for the D line and 30.1 for the F line. The difference is not large considering the somewhat arbitrary way in which we fixed the atomic refractivities.

One noteworthy feature of the optical anisotropies of individual molecules is the high values of their double refraction compared with those of crystals. For example, potassium nitrate, which is a strongly doubly-refracting crystal, has for the ratio of its principal refractive indices the value 1.587 : 1.336, i.e., 1.19 : 1, while a benzene molecule, which is also an example of a molecule with fairly high anisotropy, has for its corresponding ratio the value 2.45 : 1. The enormous decrease in the value of the anisotropy when the molecules get arranged into a crystal is due to the influence of the polarization of the atoms in the neighbouring molecules, which, being arranged on all sides of the molecule under consideration, tend to make its polarization more isotropic. A similar instance is furnished by the change in passing from benzene to cyclohexane.

#### 6. *Summary.*

Developing the idea put forward in Part I that the optical anisotropy of gaseous molecules which is responsible for the partial depolarization of the light scattered in a direction perpendicular to the incident beam, can be explained to a large extent by the mutual influence of the electrical doublets induced in the different atoms of the molecule by the electric field of the incident radiation, the optical anisotropy of benzene has been calculated for two different structures. Each atom is assumed to be isotropic. If the six carbon atoms are assumed to lie in a plane with their centres at the corners of a regular hexagon, as in graphite, the optical anisotropy comes out too high even when the hydrogens are ignored. If, on the other hand, the carbon atoms are arranged in a puckered ring, as in diamond, and the hydrogens are joined to the carbons

at the tetrahedral angle, the calculated and observed values of the optical anisotropy agree well, when the atomic refractivity of carbon is assumed to be that of diamond and the atomic refractivity of hydrogen to be that in gaseous hydrogen. The calculated and observed values of the molecular refractivity also show good agreement.

The calculation is extended to cyclohexane. The six extra hydrogen atoms are supposed to be attached to the carbon atoms alternately on each side of the approximate plane of the carbon ring. The calculation shows that a considerable falling off in anisotropy is to be expected, which is borne out by experiment. The calculated refractivity is also in fair agreement with the experimental value.

A simple glass apparatus is described for the measurement of the imperfection of polarization of the light scattered by vapours which require heating for their production.

I am very thankful to Prof. C. V. Raman for his kind and encouraging interest in the work.

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*The Adsorptive Equilibria of Binary Gaseous Mixtures.*

By WILLIAM GEORGE PALMER, Fellow of St. John's College, Cambridge.

(Communicated by Sir William Pope, F.R.S.—Received November 4, 1925.)

The method of investigating mixed adsorption films described below depends upon the following assumptions :—

- (1) That adsorption films of at least the " permanent " gases upon plane solid surfaces are usually only of unimolecular thickness.
- (2) That the so-called coefficient of reflexion of gases striking a plane solid surface is small, and may be taken in the general case as very nearly zero.
- (3) That, after condensation of a molecule of the gas owing to the action of adsorption, a considerable interval elapses before it escapes again from the surface by a process of evaporation.

These assumptions have gained general acceptance from chemists, and whatever intrinsic value the results of the present work may have is enhanced by the support they give to these conceptions.

Langmuir\* obtains the following results for the " mean life " of various

\* ' Journ. Amer. Chem. Soc., ' vol. 40, p. 1390 (1918).

molecules upon plane surfaces of mica at  $-118^{\circ}\text{C.}$ , using the formula  $s = 22,860\sqrt{MT}a$ , where  $s$  is the mean life,  $a$  the amount of adsorbed gas, and  $M$  and  $T$  the molecular weight and the temperature respectively :—

Carbon monoxide.....	10,000 seconds.
Oxygen .....	69,000   ,,
Nitrogen .....	26,000   ,,

These results are calculated from direct measurement of the adsorption  $a$ . For a number of gases the decrease of adsorption over  $100^{\circ}\text{C.}$  is of the order 0.5 to 0.1, so that at room temperature a life period on the surface of the solid of the order of 1,000 seconds is to be expected.

If the above assumptions are made, it is evident that when a mixture of two gases A and B is brought into contact with a clean surface, a unimolecular film will at once be formed ; and, if either of the two gases can be adsorbed on any part of the surface, this film will contain the gases in proportion to the ratio in which they strike the surface. If the molecular weights are respectively  $M_a$  and  $M_b$ , and the partial pressures  $p_a$  and  $p_b$ , this ratio is

$$\sqrt{M_b p_a} / \sqrt{M_a p_b}. \quad (1)$$

For an adsorption film to remain in equilibrium with the external gas mixture, the two gases must evaporate from it also in this ratio. Let the rates of evaporation be  $s_a$  and  $s_b$  when the surface is covered exclusively with the one or the other gas. Then the rate of evaporation from a surface covered to the extent  $\theta$  is  $\theta s$ . Hence the ratio in the film which will result in evaporation in the ratio (1) must be

$$\sqrt{M_b p_a s_b} / \sqrt{M_a p_b s_a}. \quad (2)$$

Hence the composition ratio of the gas film will change with time from the initial value (1) to the equilibrium value (2). If, now, some measurable variable of the surface can be found that will be a function of the composition of the film only, observed values of this variable can be set against the known initial composition, and the relation so found used to read off the composition of the equilibrium film. This is the principle of the method used in the present work, since the voltage necessary to "cohere" two fine metallic filaments has been shown to be highly specific for the gas film attached to them ('Roy. Soc. Proc.,' A, vol. 106, p. 55).

#### *Experimental.*

The apparatus was essentially the same as that described before (*loc. cit.*), with the important change that the two filaments were mounted on ground

glass stoppers so that they could be brought into mechanical contact or disjoined at will.

*Platinum Filaments* (diameter 0.025 mms.).—The most satisfactory way of cleaning these filaments was found to consist in the following consecutive operations : (1) Digestion in hot concentrated nitric acid ; (2) drying in a steam oven carefully protected from dust ; (3) a short electrical ignition in air ; (4) glowing not above low redness in the gas to be used. If the filaments cannot be heated in the gas owing to its chemical nature, then the filaments should be allowed to remain in contact with it at room temperature for some time before experiments are attempted. Platinum filaments generally behave erratically after they have been heated above about 400° in hydrogen.

The tungsten filaments used in one series of experiments were prepared by ignition *in vacuo* for a short time to a bright white heat, after which treatment they still remained pliable.

An experiment was conducted as follows : the filaments were viewed through a lens and brought into obvious mechanical contact (the amount of pressure between them has, up to reasonable limits, no observable influence on the cohering voltage) ; the filaments were then cohered with a suitable voltage, "tapped off," and an approximation to the critical voltage for the initial film then observed in a second cohering made as rapidly as possible after the tapping-off ; a number of similar observations were now made to obtain a more exact value of the initial critical voltage. The filaments were then disjoined to avoid vibrational disturbances, and allowed to stand in contact with the gas, usually for at least 12 hours. Observations of the "equilibrium" voltage were then made, the number of these being multiplied by turning the filaments into a number of different positions of contact.

Observations were made first with one of the pure gases in the apparatus. Increasing quantities of the second gas were then added, and a series of observations made. The apparatus was then pumped out, the second gas admitted, and a second series of observations made with the composition of the gas changing in the opposite sense to that in the first series. Concordant results between the two series were obtained in all cases. No special attention was paid to the total pressure, as it has already been shown that this has little or no influence on the cohering voltage with the gases used. All the recognised precautions were taken to ensure the purity of the gases. In all the experiments, except those with mixtures of nitrogen and hydrogen, for which tungsten was used, platinum filaments were used and prepared as described above.



*Carbon monoxide and oxygen.*—A series of mixtures of these two gases was chosen to test the method, as Langmuir showed (*loc. cit.*), by direct measurement of the amount of adsorbed gas, that both gases formed complete unimolecular films on "plane" platinum surfaces at room temperature. The results are shown in fig. 1, and the following data were obtained from the curves :—

Composition of the film in mol-fraction CO.

Initial.	Equilibrium.	Ratio $s_a/s_b$ (see p. 134).
0.05	0.125	3.0
0.1	0.20	2.2
0.2	0.30	2.0
0.3	0.46	2.0
0.5	0.70	2.3
0.6	0.80	2.6
0.7	0.86	2.6
0.8	0.92	2.2
0.9	0.97	2.1

In the figures the full line represents initial films, and the broken line equilibrium films.

Theoretically, a constant value for the ratio  $s_a/s_b$  would be anticipated; the experimental values in column 3 above seem to satisfy the theoretical expectation sufficiently well to support the principle of the method, and the assumptions underlying it.

*Hydrogen and carbon monoxide* (fig. 2).

Composition of film in mol-fraction  $H_2$ .

Initial.	Equilibrium.	Ratio $s_a/s_b$ .	Ratio, assuming complex CO—H <sub>2</sub> .
0.085	0.05	1.76	2.0
0.25	0.11	2.75	2.5
0.30	0.27	1.15	1.8
0.40	0.30	1.53	2.5
0.50	0.50	1.00	(complex only)
0.67	0.55	1.64	7.0
0.77	0.60	2.20	8.0
0.90	0.96	4.40	8.0
0.96	0.84	5.70	6.0

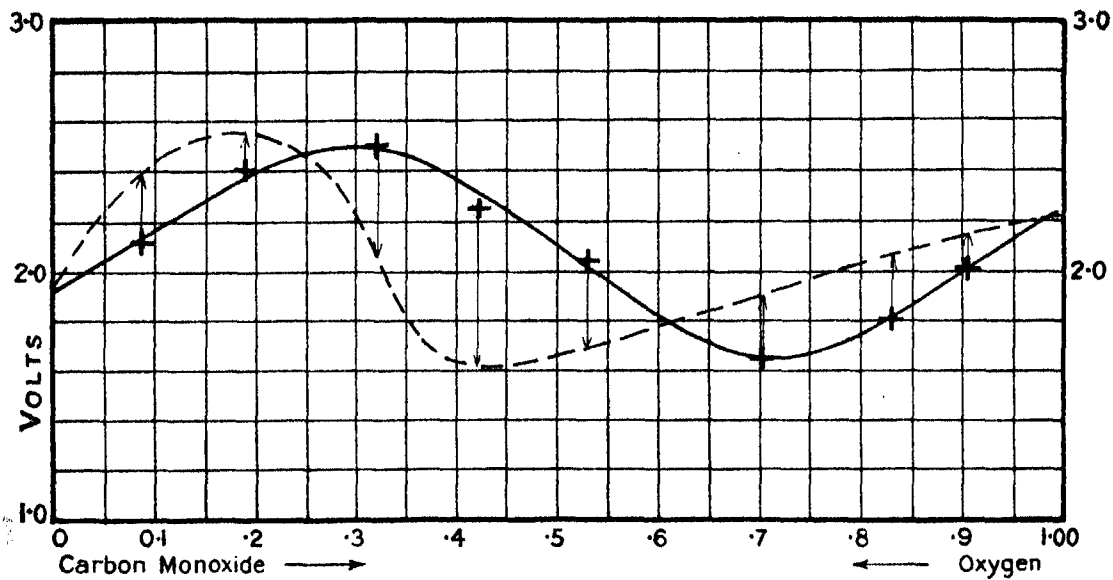


FIG. 1.

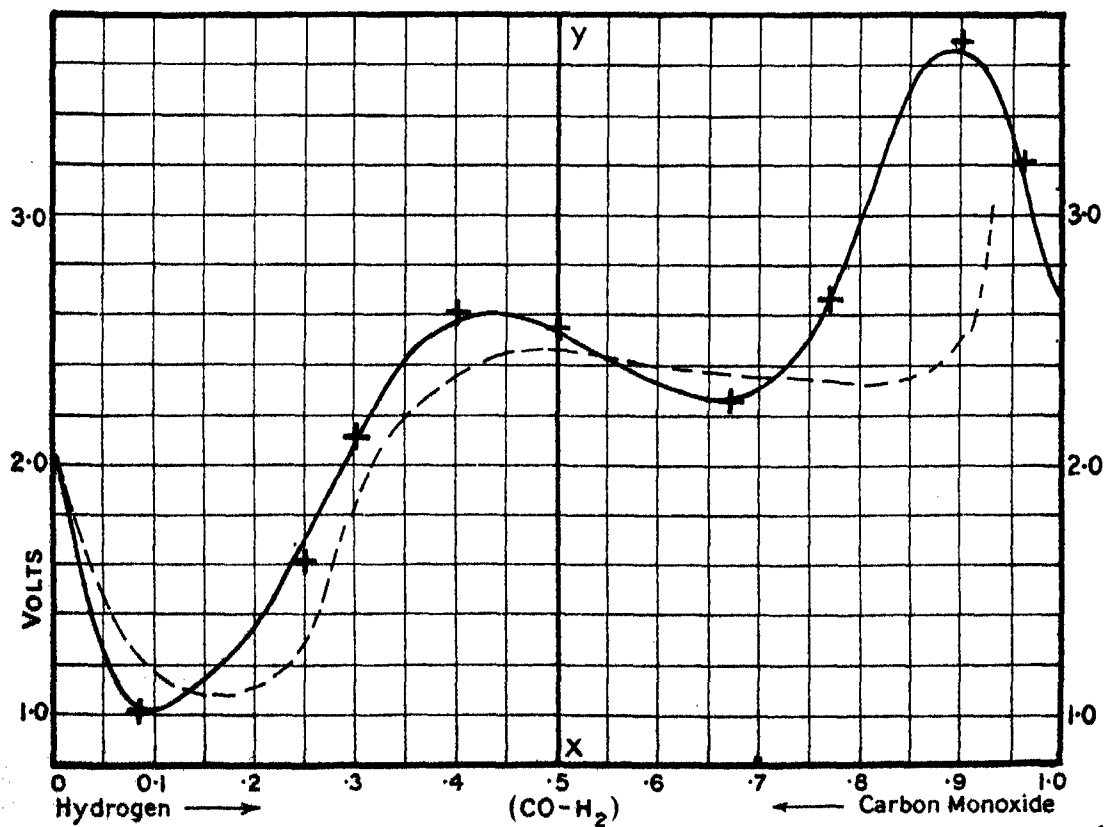


FIG. 2.

The table shows that the ratio  $s_a/s_b$  varies erratically with the composition of the mixture. The constitution of the film is, therefore, different from that of the carbon monoxide-oxygen films. The difference appears to consist in the existence on the surface of three types of adsorbed unit—hydrogen, carbon monoxide, and a complex  $\text{CO—H}_2$ , composed of one molecule of each of the gases. The evidence for this is as follows: if in fig. 2 a vertical axis  $xy$  be drawn upwards from the point  $x$  representing equal quantities of each gas in the film, and the curve be now treated as two separate curves, the one showing mixtures of  $\text{CO}$  and  $\text{CO—H}_2$ , and the other mixtures of  $\text{H}_2$  and  $\text{CO—H}_2$ , two sets of constant values of  $s_a/s_b$  ratios are obtained, corresponding to the simpler results for  $\text{CO—O}_2$  mixtures; moreover, the two halves of the complete curve resemble in form the single curve for the latter mixtures. It has been long known that formaldehyde can be synthesised in small quantities from carbon monoxide and hydrogen by the catalytic agency of platinum, and methyl alcohol is now manufactured on a large scale by a similar process. The complexes suggested are probably the precursors of actual combination, although the greater part of them must evaporate before firm chemical union takes place.

*Hydrogen Chloride and Oxygen* (fig. 3).—These mixtures were used to confirm the type of curve found for the other cases, as it appeared probable that the

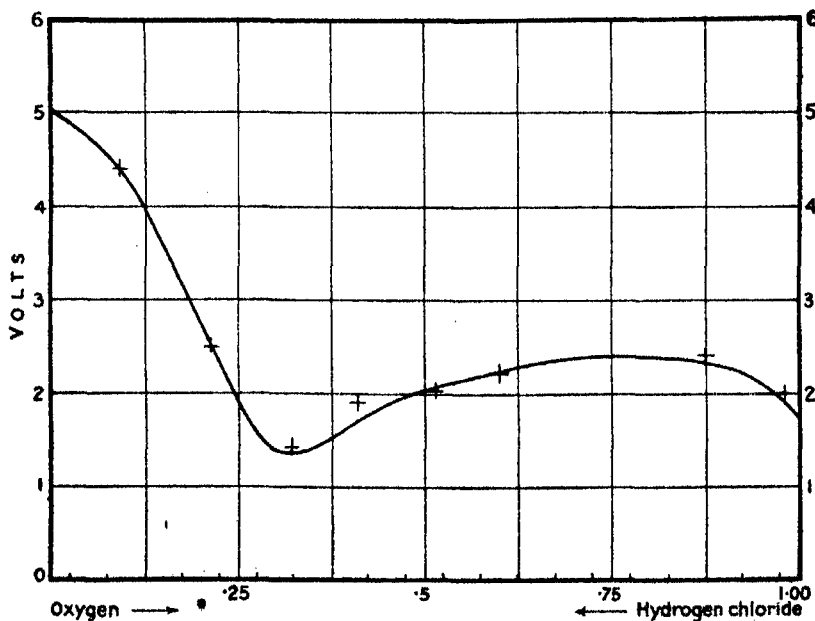


FIG. 3.

S-form was characteristic of mixtures of a polar with a non-polar gas ; the rapid decrease of cohering voltage on adding even small quantities of the non-polar to the polar gas is shown very markedly in this case.

The initial voltage for pure hydrogen chloride is 5 volts ; the voltage then rises rapidly to over 10 volts, thus indicating the formation of multimolecular films (*vide* Roy. Soc. Proc., *loc. cit.*). Hence observations of the "equilibrium" voltage could not be used to calculate  $s_a/s_b$  ratios, as the simple theory does not apply to such cases.

*Nitrogen and Hydrogen* (fig. 4).—After a number of failures some tungsten filaments were obtained that would adsorb nitrogen to a certain extent. A

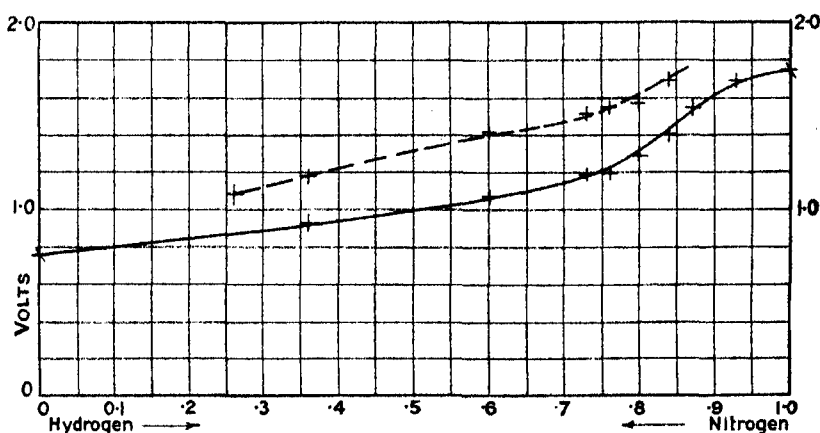


FIG. 4.

series of mixtures of this gas with hydrogen was studied with these filaments. The results have a particular interest as they show what may be expected when one of the constituents of the gas mixture does not form a complete film.

Composition of film in mol-fraction  $H_2$ .

Initial.	Equilibrium.	True Equilibrium Value.	
		(Values of Col. 3 less 0.7).	Ratio $s_a/s_b$
0.1	0.7	—	—
0.2	0.7	—	—
0.3	0.7	—	—
0.4	0.75	0.05	11.0
0.5	0.80	0.10	9.0
0.6	0.84	0.14	10.0
0.7	0.86	0.16	11.0
0.8	0.88	0.18	—
0.9	—	—	—

The apparent heat of desorption of nitrogen calculated from the cohering voltage is 180 calories per gram-mol; as the heat of evaporation of the liquid gas is approximately 1,300 calories, this low value indicates that the nitrogen is only covering a portion of the metallic surface. On the other hand, the heat of desorption of hydrogen works out to be 460 calories, while the heat of evaporation is only 160 calories, so that it may be taken that the hydrogen film is nearly complete, in the sense that the whole surface is available for the adsorption of the gas in the absence of another. Hence, even when the partial pressure of the hydrogen is low, it will be present in the film to a greater extent than would be calculated from (2).

This effect was shown experimentally in the following way. At the end of experiments in which the fraction of nitrogen had been steadily increased, an attempt was made to confirm the value for pure nitrogen, but after one exhaustion and filling with pure nitrogen a value of 1.10 volt was obtained persistently; only after numerous fillings with nitrogen was the original value of 0.75 volt obtained. Such difficulty in removing the last traces of hydrogen could not have been encountered if the nitrogen replaces this gas freely on the surface. To correct the observations for this preference of certain parts of the surface for hydrogen, a constant fraction must be deducted from the values of the "equilibrium" fraction of hydrogen. In column 4 of the above table 0.7 has been found by trial to give fairly constant values for  $s_a/s_b$ ; thus 0.7 of the whole surface is covered with "fixed" hydrogen, and it appears that although nitrogen is adsorbed on only the remaining areas, it evaporates from these about ten times as slowly as the hydrogen from other parts of the surface. This result emphasises the necessity of definite configurations of atoms on the surface to produce the phenomena of adsorption.

The values of the latent heat of desorption of mixed gas films cannot be calculated in the simple way used in the former work on pure gases (*loc. cit.*), since the dielectric constants of mixtures are insufficiently known. When the heats of desorption for pure gases are calculated from the cohering voltages found for these in the present work, the influence on the value of these latent heats of the mode of preparing the adsorbing surface becomes apparent; in the following Table, columns 1 and 3 refer respectively to tungsten and platinum filaments that have been prepared mainly by continued heating to high temperatures, and columns 2 and 4 respectively to tungsten prepared by short ignition (the filaments remaining quite pliable), and platinum cleaned in the wet way:—

Molecular heats of desorption in gram-calories.

	(1)	(2)	(3)	(4)
Nitrogen .. .. .	No	180*	—	—
	adsorption			
Hydrogen .. .. .	160	460	170	1,160
Oxygen .. .. .	—	—	1,200	1,200
Carbon monoxide ..	—	—	750	2,625
Hydrogen chloride ..	—	—	—	12,000

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*The Effect of Temperature on the Viscosity of Air.*

By FRANK ARCHER WILLIAMS, Ph.D., M.Sc.

(Communicated by Prof. H. B. Dixon, F.R.S.—Received October 7, 1925.)

The Kinetic Theory of Gases leads to a number of relations between the diffusion, conductivity and viscosity coefficients of gases, and the large measure of confirmation of these has been the greatest triumph of that theory. Most of these relations have been shown by S. Chapman† and Enskog‡ to be independent of any particular model of the molecule.

In the case of the dependence of viscosity upon temperature, however, the theory gives different results for different molecular models, and the determination of the temperature coefficient of viscosity can therefore be of service in the elucidation of molecular forces.

The Kinetic Theory as developed by Maxwell led to the relation that the viscosity should be proportional to the square root of the absolute temperature. This was deduced from the assumption that the molecules were perfectly elastic spheres between which no force was operative. Maxwell's experimental work showed, however, that the viscosity varied directly as the absolute temperature, and to explain this he was obliged to assume a repulsive force between molecules varying inversely as the fifth power of the distance. Later work showed Maxwell's experiments to be at fault, since the viscosity  $\eta$  does not increase so rapidly with temperature as Maxwell believed, although more rapidly than the square root of the absolute temperature  $T$ .

\* Apparent value calculated as though the film were complete.

† 'Phil. Trans,' A, vol. 211, p. 433 (1912); A, vol. 216, p. 279 (1915).

‡ 'Dissertation,' Upsala, 1917.

Maxwell's fifth power formula has been generalised by Brillouin,\* Chapman,† and Enskog‡ for a molecular force of repulsion varying as the inverse  $n$ th power of the distance, and leads to the relation

$$\eta \propto T^{\frac{1}{2} + \frac{2}{n-1}}, \quad (1)$$

but this has been found to hold only over a very restricted range of temperature.

An advance was made in 1893 by Sutherland,§ who put forward a formula which has met with some success. For many reasons attraction is known to exist between molecules, and Sutherland assumed it to vary inversely as some  $n$ th power of the distance. The effect of this attractive force is to bring about collisions between molecules which would not have taken place in its absence. Sutherland deduced that

$$\eta \propto \frac{T^{\frac{1}{2}}}{\left(1 + \frac{C}{T}\right)}, \quad (2)$$

where  $C$  is a constant. The agreement with the experimental results appears on the whole to be fairly satisfactory about room temperature.|| For low temperatures, however, the formula is said to show undoubted divergence from the observed values,¶ in all cases the calculated value being too small.

Two equations besides Sutherland's have been proposed for the temperature coefficient of viscosity. Reinganum\*\* started from the same physical concept as Sutherland, but by a somewhat different mathematical method he obtained the formula :

$$\eta \propto \frac{T^{\frac{1}{2}}}{e^{C/T}}. \quad (3)$$

This equation is the general case of which Sutherland's is an approximation, in which, in the expansion of  $e^{C/T}$ , all terms other than the first are neglected.

\* *Leçons sur la Viscosité des Liquides et des Gaz*, Paris, 1907.

† *Loc. cit.*

‡ *Loc. cit.*

§ 'Phil. Mag.', vol. 36, p. 507 (1893).

|| Breitenbach 'Ann. d. Phys.', ser. 4, vol. 5, p. 166 (1901); Schultze 'Ann. d. Phys.', vol. 5, p. 140 (1901); Markowski, 'Ann. d. Phys.', vol. 14, p. 742 (1904); Kleint, 'Ber. d. D. Phys. Ges.', vol. 3, p. 146 (1905); Tänzler, 'Ber. d. D. Phys. Ges.', vol. 8, p. 222 (1906); Schierloh 'Dissert. Halle,' 1908; Schmitt, 'Ann. d. Phys.', vol. 30, p. 393 (1909).

¶ Bostelmeyer, 'Ann. d. Phys.', vol. 13, p. 944 (1904); Kopsch, 'Dissert., Halle,' 1909; Rappenecker, 'Zeitschr. ph. Ch.', vol. 72, p. 695 (1910); Volker, 'Dissert., Halle,' 1910; Zimmer, 'Verh. d. D. Phys. Ges.', vol. 14, p. 471 (1912); Onnes and Weber, 'Comm. Loiden,' 1913, 134a, b and c; Vogel, 'Ann. d. Phys.', vol. 43, p. 1235 (1914).

\*\* 'Phys. Zeitsch.', vol. 2, p. 242 (1900).

On account of the inclusion of the extra terms of the expansion Reinganum's equation cannot possibly represent low temperature results so well as that of Sutherland, since the latter will always give higher values and therefore be nearer to the observations. That this is so has been shown conclusively by Rappenecker,\* Zimmer,† Onnes and Weber‡ and Vogel.§ Rappenecker attempted an empirical correction of Reinganum's formula, in which he replaced  $e^{C/T}$  by  $e^{C'/T+\alpha}$  where  $C'$  and  $\alpha$  are both constants, but this has been found no better than the original.

Quite recently J. E. Jones|| has devised an entirely new molecular model which he has shown to represent the experimental results on the temperature coefficient of argon with considerable accuracy. In this model the molecules were assumed to repel according to an inverse  $n$ th power law, and to attract according to the inverse third power. This led to the relation

$$\eta \propto \frac{T}{T^{\frac{(n-5)}{2(n-1)}} + S/T^{\frac{1}{3}}} \quad (4)$$

where  $S$  is a constant. If  $n$  be made large, we have the Sutherland relation (2). Similarly, if  $S = 0$ , we have the expression (1) for rigid molecules having no attractive force. The relation is, therefore, more general than any yet given.

Jones found that the experimental results were fitted with almost equal accuracy by any value of  $n$  from 15 to 21, with, of course, corresponding change in the value of the constant  $S$ .

It is necessary to emphasise that in the majority of the numerous researches which have been carried out on the viscosity of gases at various temperatures, and with the results of which these molecular force models have been tested, the temperature range has been severely limited. The low-temperature region has received considerable attention, but with the exception of the work of C. Barus¶ and W. J. Fisher,\*\* 300° C. represents the maximum temperature employed for any gas. The present research was primarily undertaken to extend our knowledge of viscosity over a temperature range of about 1,000° in order to obtain further data which could be applied in the consideration of molecular models.

\* *Loc. cit.*

† *Loc. cit.*

‡ *Loc. cit.*

§ *Loc. cit.*

|| 'Roy. Soc. Proc.,' A, vol. 106, p. 433 (1924).

¶ 'Ann. der Phys.,' vol. 36, p. 358 (1889); 'Bulletin U.S. Geological Survey,' No. 54 (1889).

\*\* 'Phys. Rev.,' vol. 28, p. 73 (1900).



The first investigation deals with the temperature coefficient of dry air, free from carbon dioxide.

*Experimental Method and Apparatus.*

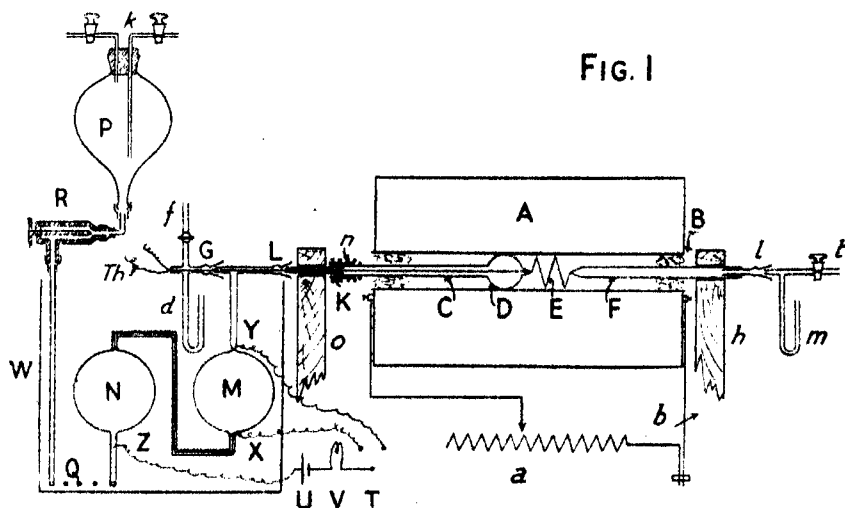
As the primary intention was to carry the investigation up to as high a temperature as possible, in the neighbourhood of  $1000^{\circ}\text{C}$ ., the difficulty of obtaining suitable materials for the construction of the apparatus at once ruled out any method of experiment other than transpiration. This requires only the capillary tube itself to be heated. Two materials for the capillary tube immediately suggested themselves--platinum and silica. Platinum capillaries were employed by Barus, but their cost is disadvantageous and, in addition, platinum may become porous at temperatures in the region of  $1000^{\circ}\text{C}$ . The upper limit that can safely be reached with a silica capillary is  $1000^{\circ}$  on account of the commencement of crystallisation of fused silica when heated for long periods at  $1100^{\circ}\text{C}$ . The smallest amount of such crystallisation would be fatal to the method. A silica capillary, moreover, possesses the advantage that its coefficient of expansion is so extremely small that the variation in bore of the capillary over a range of temperature of  $1000^{\circ}$  was shown by calculation to be negligible. Silica capillary, however, cannot be obtained of perfectly uniform bore, so that resort was made to a comparative method.

The general method of experiment was as follows. A known volume of the gas was displaced from a glass bulb immersed in a thermostat, by means of a stream of mercury which flowed in from a reservoir. The displaced gas transpired through the silica capillary, heated in an electric furnace, and thence passed out into the free atmosphere. By controlling the rate of flow of the mercury into the bulb, the pressure in the latter could be kept at any desired value throughout the experiment. A comparison of the times required for equal volumes of gas to transpire through the capillary under the same driving pressure, when the capillary was heated at different temperatures, enabled one to compare the viscosities of the gas at these temperatures.

A diagrammatic sketch of the apparatus is given in fig. 1. A is an electric resistance furnace, 3 feet long and of 15 inches cross-section, consisting of a box of "Uralite" supported in an iron frame, through which passes centrally a large vitreosil tube B of 3-inch bore. The outside of B is wrapped with asbestos paper, and wound with one layer of No. 17 nichrome wire. This coil is covered with asbestos paper, and one small coil about 6 inches long placed at each end of B over the first winding. These small coils are connected

in series with one another and with the main coil, and serve to keep the ends of the furnace hot, so maintaining a uniform temperature along the tube. The furnace is connected with the 240-volt mains through a variable resistance *a* and an ammeter *b*. Both ends of B are packed tightly with slag wool.

The silica apparatus, C, D, E, F, was made by the Thermal Syndicate. It consists of a piece of transparent silica tube C, of  $\frac{3}{4}$ -inch bore and 28 inches long, having a bulb D,  $2\frac{1}{2}$  inches in diameter at one end, and tapering to the capillary E, also of transparent quartz. The capillary E, 0.4 mm. in bore and 61 cm. long, is wound in a spiral of  $2\frac{1}{2}$  inches external diameter and  $\frac{1}{2}$ -inch pitch, and is joined to a piece of opaque silica tube F, of  $\frac{3}{4}$ -inch bore and 2 feet long. The bulb has a most important function, viz., that of ensuring that the



gas should become heated to the temperature of the furnace before actually reaching the capillary E. This pre-heating bulb was made spherical, for reasons of mechanical strength and for ensuring that the driving pressure at the commencement of the capillary should be that measured by the manometer *d*. With any other form of pre-heater—for example, a spiral of tubing—there would be a certain amount of back-pressure unless it were made of very wide bore. As the bulb D was of about 250 c.c. capacity, the time taken for the gas to flow across was considerable, and in the actual experiments no cooling of the thermojunction *Th* could be detected when the flow of gas was commenced, showing that the pre-heating was sufficient.

Before the silica apparatus, C, D, E, F, was inserted into the furnace tube, it was thoroughly cleaned with a mixture of potassium bichromate solution

and sulphuric acid, then washed repeatedly with distilled water, thirdly with alcohol, and finally with ether, and the ether removed by drawing air through the apparatus. The handling of this extremely fragile and awkwardly-shaped apparatus (nearly 4 feet long) for the purpose of washing was a matter of great difficulty, and was finally accomplished by fastening the apparatus to a board with lead straps. The insertion of C, D, E, F into the furnace tube was an even more delicate operation, which involved the sliding of the apparatus off the board and along the furnace tube. Once in the furnace, fireclay rests were placed under C and F. The ends of the silica apparatus were clamped in the wooden stands *o* and *h*. Half of a ground joint *l* was joined to F by a rubber bung, which was coated with Faraday cement. The other half of this joint carried a tap *t* and a side-arm connection for a mercury manometer *m*.

By means of a butt joint K one half of a  $\frac{1}{2}$ -inch bore ground joint L was attached to C. The butt joint was made from a piece of brass tube 3 inches long, into which the tubes were cemented with a mixture of litharge and glycerine. The joint was carefully covered with Faraday cement to render it gas-tight, and in order that the Faraday cement should not be softened by heat radiated from the furnace, the joint K was cooled by passing water through a spiral *n* of "compo tubing" wound round it. The other part of the joint L was fused to the volume measuring apparatus M, N, which was supported in a frame, adjustable to any height, immersed in a thermostat W, which was maintained at a temperature of 25° C. The two bulbs M and N were each of about 600 c.c. capacity in the early experiments. Later on, 300 c.c. bulbs were substituted in order to reduce the time of an experiment.

Connection between M and N was made with 2 mm.-bore capillary tubing. A platinum contact X was sealed into the bottom of M. The tube at the top of M was constricted to  $\frac{1}{8}$  inch and another platinum point Y was inserted here. The points of both X and Y were directed downwards. A third contact Z was fused into the bottom of N. Z was connected through an accumulator U and a "pea" lamp V to the arm of a two-way switch T. The poles of T were connected to X and Y. In the earlier experiments contact was made between T and the platinum X, Y and Z, with cotton-covered copper wire twisted round the loops on X, Y, and Z. Bad corrosion of the wire, however, took place on account of the immersion in water in W, and set up considerable resistance between the wire and the platinum. These leads were replaced later with enamelled copper wire, and contact was made with the platinum by twisting the wire through the loops and casting on top of this a mass of Wood's metal.

This proved extremely satisfactory, since no corrosion took place in six months, and it also served to protect the platinum wire from mechanical strain. The volume between the contacts X and Y had been accurately determined by calibration. For this purpose a stopcock was fused to the bottom of N. M and N were then completely filled with mercury. Mercury was run out from the stopcock until contact of the mercury with the platinum point Y was just broken, as indicated by the lamp V ceasing to glow. Sufficient mercury was then run out until contact was no longer made by the mercury at X. The quantity of mercury required to fill the bulb M, between X and Y, was determined by weighing on a special large balance, accurate to less than 0.1 gm. with 2 kgm. on each pan. The weights used were Becker's, of guaranteed accuracy. The mercury was of necessity weighed in several instalments, and the temperature of the room during the calibration was noted. The calibration was repeated several times and the mean weight of mercury used to calculate the volume of M.

G is a small ground-glass cap having two small holes in its end, through which passed the wires of the thermocouple *Th*. The wires were sealed into G with Faraday cement. The cold junctions of the couple were placed in test-tubes immersed in the thermostat W. The hot junction rested close against the end of the capillary spiral E. One wire of the couple was enclosed in a piece of small-bore silica tubing for insulation from the other wire, which was left exposed. The cap G carried two side-arms. An oil manometer *d* was joined through a glass spiral and ground joint to one of these. The oil used was Fleuss-pump oil with a very low vapour pressure. The density of the oil was determined by means of a pycnometer at several different temperatures, and a curve of density against temperature prepared, on which the density at any particular temperature could be read. Opposite this side-arm *d* was the tube *f*, which was the inlet tube for the gas to be investigated. As dry air free from carbon dioxide was the first gas studied in this research, the tube *f* was connected by ground-glass joints to a battery of three large tubes, each 50 cms. long and 4 cms. bore. The incoming air first passed through one of these, which contained pieces of well-broken stick caustic potash to remove carbon dioxide, then through a large tube of granular calcium chloride, to dry the air partly, and finally through a tube containing glass-wool sprinkled with phosphorus pentoxide to complete the drying.

The mercury reservoir P was of 1,200 c.c. capacity. The rate of flow of mercury from it was controlled by the needle valve R, which was made of iron to prevent amalgamation. After leaving R the mercury flowed through

a coil *Q* to take the temperature of the thermostat *W*. The reservoir *P* was fitted as a Mariotte's bottle, by having a fine capillary point *k* which dipped below the surface of the mercury, in order to make the need to adjust *R* as infrequent as possible.

The thermocouple *Th* consisted of a platinum—10 per cent. rhodium platinum junction. The E.M.F. produced by the junction was balanced on a bridge wire in the usual manner. The bridge was capable of readings of an accuracy of about five microvolts.

The thermocouple was calibrated directly by using the following standard temperatures :—

	° C.
Boiling point of water .....	100
„ „ naphthalene .....	218
„ „ sulphur .....	444.5
Melting points of tin .....	232
„ „ cadmium .....	321
„ „ zinc .....	419
„ „ antimony .....	630
„ „ salt (pure).....	801
„ „ silver .....	961

The calibration results at standard temperatures were corrected for the cold junction and the results were plotted against temperature on a large scale graph, from which the temperature corresponding to any particular E.M.F. could be readily obtained.

The hot junction of the thermocouple *Th*, fig. 1, rested in the tapered tube between the bulb in the silica tube and the silica capillary spiral itself, and as close to the spiral as possible without interfering with the flow of gas.

Before use the apparatus was tested for gas-tightness. All ground-glass joints in the apparatus were carefully coated with a layer of Faraday cement. Stopcock *f*, that on *d* and the valve *R*, were closed. The apparatus was evacuated through *t*, and by observing the level of the mercury in *m*, the apparatus was found to be satisfactorily gas-tight. During the course of the experiments the apparatus was periodically tested.

The stop-watch used was made by J. W. Benson, of London, and was non-magnetic, as it was to be employed near the heavy current in the electric furnace. It was always placed in the same position during the experiments. The watch was checked against the wireless time signal from Greenwich.

All barometer readings were taken on a Fortinette standard barometer of bore 6.3 mm., of which the capillary depression was found by Landolt-Börnstein's tables to be 0.052 cms.

The method of performing an experiment was briefly as follows :—Tap *f* was closed and the piece carrying the stop-cock *t* was removed from the joint *l*. By opening the valve *R* a suitable amount, mercury flowed from *P* into *MN* and set up a pressure therein, which was measured in the manometer *d*. The use of the bulb *N* is now seen. While *N* was filling with mercury constant pressure was maintained in the apparatus by observing the manometer *d* and adjusting *R* accordingly, and the temperature gradient along the tube *C* also reached a stable value, so that by the time the mercury level made contact at *X*, which was put in circuit by means of the switch *T*, conditions were suitable for making a timed observation. The barometer was read just before the mercury reached *X* and its temperature noted. Barometer observations were repeated at intervals, usually of about twenty minutes, depending on the duration of the experiment, during the timed period. The time at which the lamp *V* lighted was noted by the stop-watch. The switch *T* was then swung over so as to put the contact *Y* in circuit, and the time observation repeated when the lamp *V* was again lighted. Readings of the manometer *d* and its temperature were also made at intervals during the experiment. A known volume of gas had therefore left *M* under a measured pressure and transpired through the capillary *E*, at a temperature given by the thermocouple *Th*, during a time given by the stop-watch.

To render the apparatus ready for another experiment *R* and *k* were closed and *f* opened. The tube with the tap *t* was inserted into *l* and *t* closed. By means of a water-pump the reservoir *P* was exhausted and the mercury was thus sucked back into *P*. The low pressure produced in *M* and *N* drew in through *f* a fresh supply of the gas under investigation. The tube *F* was closed to prevent air being drawn back through the capillary *E* into *N* and *M*. Upon closing *f*, opening *k*, and removing the piece *t*, the apparatus was ready for a fresh experiment.

With the apparatus as thus described the experimental results of Tables I, II and III were obtained.

#### *Theory of Method.*

The method employed in the research was first to determine what may be called the constant *K* of the capillary by making a number of experiments

at room temperatures, using a gas of known viscosity. The following equation deduced by O. E. Meyer\* applies to each of these experiments:—

$$\eta_1 = \pi \cdot \tau_1 \cdot \frac{p_1^2 - p_2^2}{2p_1} \cdot \frac{R^4}{8V_1L} (1 + 4\xi_1/R) \quad (5)$$

where  $\eta_1$  is the coefficient of viscosity in C.G.S. units at the temperature  $t_1^\circ$  of the experiment,  $\tau_1$  the time of flow through the capillary of a volume  $V_1$  of gas measured at the inlet pressure  $p_1$ ,  $p_2$  the outlet pressure,  $R$  the radius and  $L$  length of the capillary, and  $\xi_1$  the coefficient of slip of the gas along the walls of the tube.

This equation may be written

$$\frac{R^4}{L} = \frac{16\eta_1 V_1 p_1}{\pi \tau_1 (p_1^2 - p_2^2)} \cdot \frac{1}{(1 + 4\xi_1/R)} \quad (6)$$

Now  $R$  cannot be determined accurately, so we must regard  $R$  as the mean value along the capillary. The approximate value of  $R$  is sufficiently accurate for use in the slipping correction  $(1 + 4\xi/R)$ , as this term is small.

If now the capillary be heated to the temperature  $t_2$ , and the experiment is repeated, then, assuming  $R$  remains constant,

$$\eta_2 = \pi \tau_2 \frac{(p_3^2 - p_4^2)}{2p_3} \frac{R^4}{8V_2L} (1 + 4\xi_2/R) \quad (7)$$

where  $\eta_2$  is the new coefficient of viscosity,  $\tau_2$  the time of transpiration of the volume,  $V_2$  of gas through the capillary at  $t_2$  from the pressure  $p_3$  to the pressure  $p_4$ , and  $\xi_2$  is the new coefficient of slip.

Dividing (7) by (6)

$$\begin{aligned} \eta_2 &= \frac{\tau_2}{V_2} \frac{(p_3^2 - p_4^2)}{p_3} \cdot \frac{(1 + 4\xi_2/R)}{(1 + 4\xi_1/R)} \cdot \frac{\eta_1 V_1 p_1}{\tau_1 (p_1^2 - p_2^2)} \\ &= \left\{ \frac{\tau_2}{V_2} \frac{(p_3^2 - p_4^2)}{p_3} (1 + 4\xi_2/R) \right\} \left( \frac{\pi}{16} \cdot \frac{R^4}{L} \right) \\ &= \left\{ \frac{\tau_2}{V_2} \cdot \frac{(p_3^2 - p_4^2)}{p_3} (1 + 4\xi_2/R) \right\} K. \end{aligned} \quad (8)$$

Hence  $\eta_2$  can be calculated.

#### *Determination of the Capillary Constant K.*

In deciding which gas was to be used as the standard for the calibration, it was apparent that the researches on the viscosity of air far exceeded in number and estimated accuracy those on any other gas. Air was, therefore,

\* 'Pogg. Ann.,' vol. 127, p. 263 (1866).

chosen as the calibrating gas. Critical summaries of the value of  $\eta$  for air at 23° C. and at 0° C. respectively have been made by R. A. Millikan\* and H. Vogel.† Millikan selects what he considers the five most accurate observations and takes a mean of these :—

Observer.	Method.	C.G.S. Units.
Rapp (§) .....	Transpiration.....	0·00018227
Gilchrist (§) .....	Constant deflection .....	0·00018257
Hogg (  ) .....	Damping of oscillating cylinders ..	0·00018229
Tomlinson (§§) .....	Damping of pendulums .....	0·00018258
Grindley and Gibson (**)	Transpiration through large tube..	0·00018232

$$\text{Mean } \eta_{23}^{\circ} = 0\cdot00018240$$

Millikan estimates the error in this to be less than one in a thousand.

Vogel collects the results of each method of experiment together and finds the mean of all the results by each method, excluding a few which are obviously incorrect. To each method Vogel then assigns a number which he considers represents the value of the method from the point of view of accuracy, and this is taken into account in evaluating the mean of all the methods. Vogel finds  $\eta_0 = 1724 \cdot 10^{-7}$ .

He estimates the accuracy of the mean to be 0·5 per cent. Much of the data used was not obtained at 0° C., but about 15° to 20° C., and was reduced to 0° C. by using Sutherland's formula, in which Vogel substituted a value of  $C = 117$ , which is the mean value of  $C$  as determined by several experimenters. This value of  $\eta_0$  contains many results which are most probably in error, as no really critical attempt was made to choose the more accurate of the original data. Millikan, on the other hand, calculated his values for 23° C. from data obtained at temperatures only a few degrees different, by using an empirical factor, which was obtained from the work of Gilchrist,†† Rapp,†† Fisher,†† Schultze,†† and Hogg,†† all of whom agreed in this particular. Millikan's final formula was  $\eta_t = 0\cdot00018240 - 0\cdot000000493 (23^{\circ} - t)$ , which he estimated to be correct to one part in a thousand over the temperature range

\* 'Ann. d. Physik,' vol. 41, p. 759 (1913).

† 'Ann. d. Physik,' vol. 43, p. 252 (1914).

‡ 'Phys. Rev.,' vol. 2, p. 363 (1913).

§ 'Phys. Zeitschr.,' vol. 14, p. 161 (1913).

|| 'Amer. Acad. Proc.,' vol. 40, p. 609 (1905).

§§ 'Roy. Soc. Proc.,' vol. 40, p. 40 (1886).

\*\* 'Roy. Soc. Proc.,' A, vol. 80, p. 114.

†† *Loc. cit.*



$t = 12^\circ$  to  $t = 23^\circ$ . If we assume  $C = 117$  in Sutherland's formula, Millikan's value at  $23^\circ$  reduces to  $1710 \cdot 10^{-7}$  at  $0^\circ \text{C.}$ , as compared with Vogel's value of  $1724 \cdot 10^{-7}$ .

Millikan's value has, however, been amply confirmed by a very accurate determination by Harrington,\* for use in the calculation of the value of the electronic charge,  $e$ , which is limited in its accuracy by that with which  $\eta$  is known. Harrington obtained  $\eta_{23^\circ} = 1822 \cdot 6 \times 10^{-7} \pm 0 \cdot 05$  per cent. Millikan's expression for  $\eta$  has, therefore, been adopted in this work, as its accuracy is probably of the order of 1 in 1000.

#### Experimental.

The silica capillary was heated to about  $500^\circ \text{C.}$  in order to dry it thoroughly. The apparatus M and N was evacuated and filled with pure, dry air several times. After allowing to cool to room temperature a number of experiments were carried out as detailed above. The temperature of the capillary was determined for this calibration by means of a calibrated mercury thermometer accurate to  $0 \cdot 1^\circ \text{C.}$ , inserted into the furnace. The temperature of the thermostat was then adjusted so as to be exactly equal to that of the capillary.

The first capillary tested did not give concordant results and was rejected. A second and more uniform capillary yielded the values given in Table I.

Table I.

$p_1 - p_2$ dynes.	$p_2$ dynes.	$V_1$ c.c.	$t_1$ Temp. of capillary.	$\eta_1 \cdot 10^4$	$\tau_1$	$K(1 + 4\xi_1/R)$ .
73550	1021400	629.60	15.0	1.7846	975.2	8.1040
73380	1020900	629.60	15.0	1.7846	977.0	8.1078
73450	1020600	629.60	15.1	1.7851	976.0	8.1114
73410	1020400	629.60	15.3	1.7880	977.6	8.1067
73430	1020200	629.60	15.2	1.7856	977.2	8.1058
73780	1034000	629.52	9.7	1.7584	959.2	8.0898
73750	1033800	629.53	10.1	1.7604	958.6	8.1077
73840	1033800	629.53	10.2	1.7609	959.0	8.0973
73840	1034000	629.53	10.3	1.7614	958.0	8.1077
73280	1008800	629.59	14.0	1.7796	975.0	8.1159
73550	999300	629.59	14.5	1.7821	971.0	8.1334
73510	998800	629.59	14.5	1.7821	972.0	8.1294
73470	998700	629.59	14.5	1.7821	972.4	8.1307
73720	1014000	629.54	11.1	1.7654	960.0	8.1268
73690	1013800	629.54	11.1	1.7654	963.0	8.1055
73710	1013600	629.54	11.1	1.7654	962.0	8.1120
73690	1013100	629.54	11.1	1.7654	962.0	8.1138
73680	1013000	629.54	11.1	1.7654	963.0	8.1068

Therefore, mean value of  $K(1 + 4\xi_1/R) 10^{10} = 8.1118$ .

\* 'Phys. Rev.', vol. 8, p. 738 (1916).

Under  $p_1 - p_2$  are the values of the oil driving pressure in dynes.  $V_1$  is calculated from the volume  $V_0$  of the bulb M at  $0^\circ \text{C}$ . by

$$V_1 = V_0 (1 + \beta t_1)$$

where  $\beta$ , the coefficient of expansion of ordinary soda glass, is taken to be 0.000024 in this work,  $t_1$  is the temperature of the thermostat, which for the calibration experiments is equal to that of the capillary. Under  $\eta_1$  are the values calculated from Millikan's equation. In the last column are the values of  $K$  without regard to the slipping coefficient. The mean value of  $(1 + 4\xi_1/R) K$  has now to be corrected for slip.

*Correction for Slip.*

This correction occurs as the factor  $(1 + 4\xi/R)$  where  $\xi$  is known as the coefficient of slip. Kundt and Warburg\* showed experimentally that  $\xi$  was directly proportional to the mean free path  $\lambda$  of the molecules. Meyer deduced theoretically that

$$\xi = \lambda,$$

and, in order to correct for  $\xi$ , most experimenters have calculated the value of  $\lambda$  and substituted directly in  $(1 + 4\xi/R)$ . Theoretical work by Knudsen,† confirmed by some careful experimental work, resulted in the formula

$$\xi = \frac{8\sqrt{2}}{3\sqrt{\pi}} \cdot \frac{\eta}{\sqrt{p\rho}} \cdot C_1/C_2, \quad (9)$$

where  $\rho$  = specific gravity of the gas at the temperature of the experiment  
 $p$  = mean pressure along the capillary, and  $C_1/C_2$  is a number which Knudsen's experiments gave as 0.81. Knudsen's work has been confirmed by Gaede.‡ It will be seen that by putting

$$\xi = k\lambda \quad \text{or} \quad \lambda = \xi/k,$$

$k$  can be found by substituting for  $\lambda$  in the equation of the simple Kinetic Theory

$$\eta = \frac{1}{2} \rho v \lambda \quad (10)$$

where  $v$  is the mean velocity of the molecules. If, with Knudsen, the equation

$$\eta = 0.3097 \rho v \lambda \quad (11)$$

\* 'Pogg. Ann.,' vol. 155, pp. 337 and 525 (1875).

† 'Ann. der. Phys.,' vol. 28, p. 75 (1909).

‡ 'Ann. der Phys.,' vol. 41, p. 337 (1913).

be used, which is (10) as corrected for the Maxwell Distribution of Velocities, then

$$\xi = 0.85 \lambda. \quad (12)$$

Equation (11) has been corrected by Jeans,\* who agrees with further corrections by Chapman† which make

$$\eta = 0.499 \rho v \lambda \quad (13)$$

which has also been confirmed by Enskog.‡ On this basis

$$\xi = 1.41 \lambda. \quad (14)$$

In the present work,  $\xi$  has been calculated for each experiment, directly from (9) to avoid being dependent upon the value of the coefficient in (10).

The mean pressure  $p$  is obtained by substituting in Kundt and Warburg's formula

$$p = \frac{p_1^2}{p_1 + (p_1 - p_2)}$$

where  $p_1$  is the initial pressure and  $p_2$  the final pressure of the gas.

On account of the large bore of the capillary used in the present research, 0.04 cms., the value of the factor  $(1 + 4\xi/R)$  at 1000° C. differs from unity by only about 0.009, and it was for this reason that such a large tube was employed.

The apparent value of the radius of the capillary for use in calculating the slipping correction was obtained in the following way. From (8)  $K = \frac{\pi}{16} \cdot \frac{R^4}{L}$ , therefore  $R^4 = \frac{16KL}{\pi}$ .

Now from Table I,  $K = 0.008112$  (neglecting slip),

and

$$L = 61 \text{ cms.}$$

Hence

$$R = 0.0224 \text{ cms.}$$

For each of the calibration experiments in Table I all the terms required to calculate  $\xi_1$  are the same to two figures, and it is sufficient to correct for slip the mean value of  $K (1 + 4\xi_1/R)$ .

Hence  $\xi_1 = 0.0090$  cms., and  $4\xi_1/R = 0.0016$ ,

$$\therefore (1 + 4\xi_1/R) = 1.0016,$$

and  $K$  from Table I = 0.0080988.

\* 'Dynamical Theory of Gases' (1921).

† 'Phil. Trans.,' A, vol. 216, p. 279 (1915).

‡ *Loc. cit.*

*High Temperature Measurement.*

Table II contains the results, in chronological order, of a number of experiments obtained when the volume of the bulb M (fig. 1) was 629.75 c.c. at 25° C. The thermostat W (fig. 1) was maintained throughout the results of Tables II and III at 25° ± 0.1° C. The values under  $V_2$  therefore represent

$$\frac{629.75}{(1 + \alpha 25)} (1 + \alpha t_2),$$

where  $\alpha$  is the coefficient of expansion of air which was taken as 0.000367;  $p_3 - p_4$  is the oil pressure in dynes;  $p_4$  the barometric pressure;  $\tau_2$  the duration of the experiment;  $t_2$  the temperature in ° C.

The column under  $\frac{\eta_2}{1 + 4\xi_2/R}$  represents the viscosity uncorrected for slip, and that under  $\eta_2$  the corrected values.

Table II.—Air.

$p_3 - p_4$	$p_4$	$V_2$	$\tau_2$	$t_2$ °C.	$\frac{\eta_2 \cdot 10^4}{1 + 4\xi_2/R}$	$\eta_2 \cdot 10^4$
73050	1003300	1702.9	5417	532	3.636	3.656
73120	1003100	1724.1	5503	542	3.652	3.672
73080	992700	1838.4	6217	596	3.865	3.888
73050	990100	1844.8	6259	599	3.876	3.900
72960	993400	2058.6	7428	700	4.118	4.146
72980	1004400	2181.4	8221	758	4.304	4.335
73290	986700	1389.7	3883	384	3.202	3.216
73230	986700	1396.0	3911	387	3.208	3.222
73060	995600	1618.3	5064	492	5.576	3.594
73080	998300	1626.8	5079	496	3.570	3.588
72920	1007900	1840.6	6241	597	3.870	3.893
73060	1010800	2012.1	7215	678	4.100	4.127
73430	1026400	1336.7	3558	359	3.060	3.072
73290	1026400	1345.2	3591	363	3.063	3.075
73400	1028400	1601.4	4890	484	3.509	3.527
73380	1027900	1614.1	4943	490	3.519	3.537
73440	1005700	1690.3	5286	526	3.603	3.622
73260	1025100	1923.1	6623	636	3.950	3.975
73610	1024400	976.87	2103	189	2.481	2.488
73560	1023100	983.21	2123	192	2.487	2.493
73510	1023100	987.48	2138	194	2.492	2.499
73450	1017700	1262.7	3275	324	2.982	2.993
73360	1017200	1271.2	3315	328	2.995	3.006
73290	1017600	1277.5	3342	331	3.001	3.012
73360	1025600	1168.1	2827	279	2.780	2.790
73270	1029400	1171.6	2859	281	2.800	2.809
73210	1031100	1175.9	2857	283	2.786	2.795

In Table III, the results were obtained with a smaller bulb M of 297.97 c.c. at 25° C. The object of this change was to reduce the time of experiment.  $\bar{V}_2$  in this case is equal to

$$297.97 \frac{(1 + \alpha t_2)}{(1 + \alpha 25)} \text{ c.c.s.}$$

Table III.

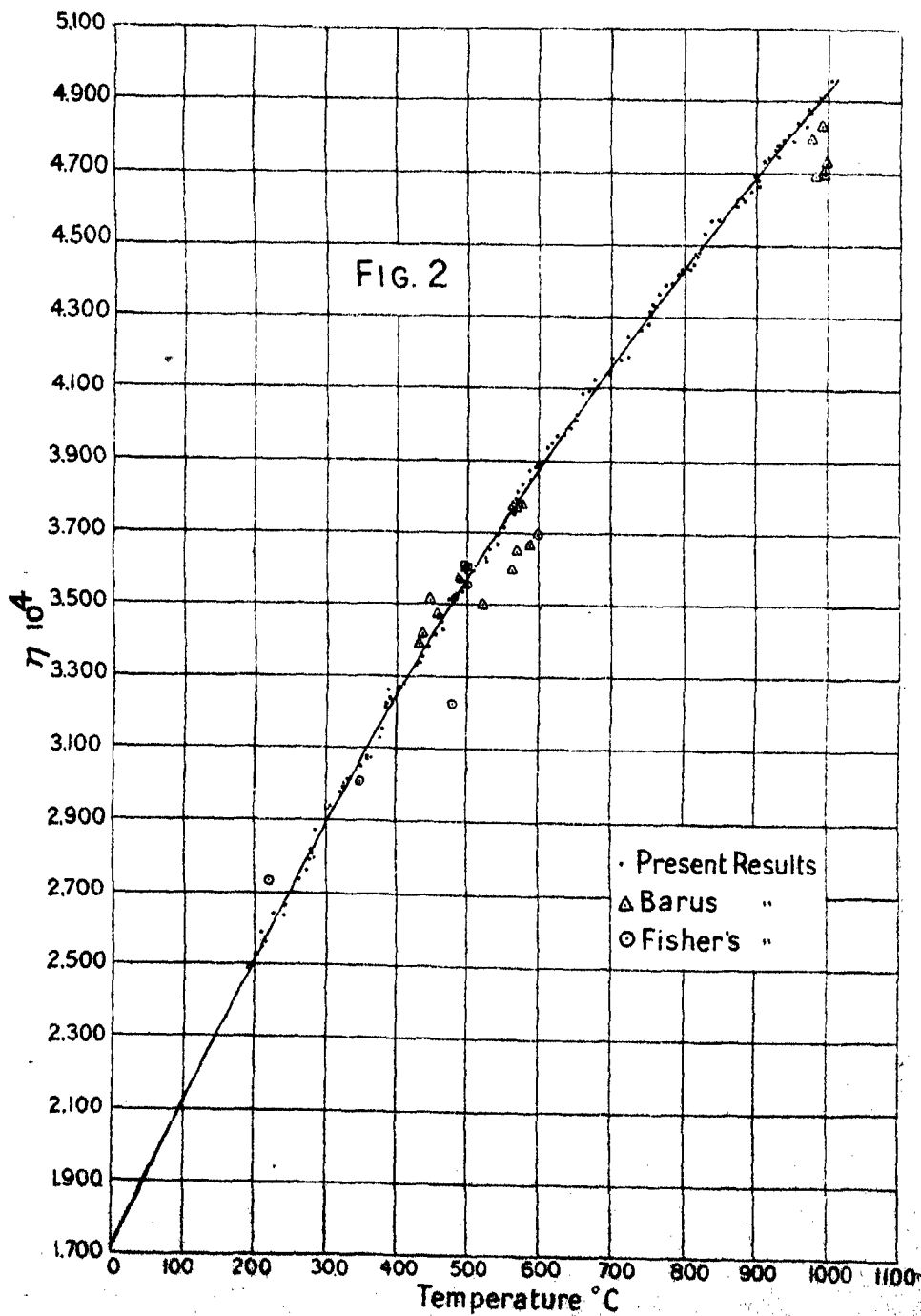
$p_3 - p_4$	$p_4$	$V_2$	$\tau_2$	$t_2^\circ \text{C.}$	$\frac{\eta_2 \cdot 10^4}{1 + 4\zeta_2/R}$	$\eta_2 \cdot 10^4$
73200	1022100	841.83	2770	568	3.774	3.795
73210	1021000	843.82	2790	570	3.789	3.811
73260	1009800	1004.2	4244	820	4.447	4.480
73200	1008300	1090.2	4230	816	4.444	4.478
73210	1007400	1092.2	4233	818	4.440	4.473
73210	997000	1173.3	4767	899	4.654	4.695
73220	993600	1175.4	4765	901	4.643	4.685
73260	996800	1220.4	5066	946	4.763	4.808
73200	997200	1220.4	4946	928	4.710	4.754
73220	998100	1205.4	4952	931	4.706	4.750
73240	987500	1154.3	4626	880	4.590	4.630
73200	986100	1148.3	4597	874	4.583	4.623
73430	1000400	554.37	1356	281	2.810	2.819
73380	1000900	558.36	1394	285	2.866	2.876
73290	1001100	575.39	1466	302	2.922	2.932
73410	1006400	661.55	1860	388	3.245	3.259
73310	1007100	652.51	1784	379	3.137	3.150
73300	1010600	761.71	2365	488	3.661	3.580
73350	1010300	777.73	2433	504	3.591	3.609
73400	1012800	838.83	2732	565	3.741	3.762
73330	1012000	836.81	2724	563	3.736	3.757
73330	1011900	837.82	2727	564	3.735	3.756
73290	986400	891.91	3052	618	2.922	3.948
73230	989700	925.95	3222	652	3.985	4.013
73240	988100	923.95	3214	650	3.984	4.011
73170	985100	935.96	3320	662	4.059	4.087
73150	984700	943.99	3357	670	4.068	4.097
73220	972200	972.04	3493	698	4.113	4.140
73190	970800	988.06	3586	714	4.152	4.180
73180	969700	998.08	3632	724	4.165	4.193
73120	980700	1026.1	3815	752	4.251	4.281
73600	1023100	546.35	1306	273	2.754	2.763
73590	1023200	536.33	1270	263	2.728	2.737
73450	1023400	526.32	1232	253	2.692	2.700
73500	1023700	514.31	1175	241	2.628	2.637
73540	1024400	490.26	1088	217	2.555	2.562
73570	1025100	481.26	1061	208	2.539	2.547
73570	1031300	674.56	1892	401	3.233	3.248
73550	1031200	678.58	1918	405	3.255	3.269
73490	1030500	701.61	2022	428	3.316	3.332
73460	1030800	704.61	2036	431	3.324	3.339
73340	1029700	708.62	2063	435	3.344	3.359
73310	1028800	717.63	2103	444	3.364	3.360
73240	1027200	726.64	2152	453	3.397	3.413
73240	1018200	736.65	2204	463	3.430	3.447
73130	1016300	767.71	2381	494	3.556	3.568
73210	1015900	784.74	2456	511	3.586	3.605
73130	1029300	1040.1	3936	766	4.334	4.365
73030	1029100	1035.1	3890	761	4.296	4.329
72990	1028800	1028.1	3857	754	4.288	4.319

Table III—(contd.).

$p_s - p_d$	$p_d$	$V_s$	$\tau_s$	$t_s$ °C.	$\frac{\eta_s \cdot 10^4}{1 + \alpha \xi_s/R}$	$\eta_s \cdot 10^4$
73030	1022400	1047.1	3986	773	4.353	4.384
72990	1023200	1057.2	4035	783	4.362	4.395
72960	1023600	1066.2	4094	792	4.387	4.420
73120	1028400	1072.2	4116	798	4.396	4.429
73080	1029200	1078.2	4151	804	4.406	4.439
73060	1029900	1082.2	4165	808	4.404	4.437
73100	1030700	1087.2	4193	813	4.416	4.449
73110	1029100	1103.2	4337	829	4.501	4.536
73050	1027600	1113.2	4410	839	4.532	4.568
73030	1025500	1123.3	4454	849	4.535	4.570
73190	1029400	1140.3	4544	866	4.567	4.604
73200	1029600	1148.3	4585	874	4.577	4.614
73240	1029800	1158.3	4633	884	4.587	4.625
73220	1032800	1167.3	4697	893	4.614	4.652
73160	1032000	1178.4	4761	904	4.629	4.668
73110	1031400	1186.4	4870	912	4.699	4.739
73170	1032400	1194.4	4900	920	4.701	4.741
73130	1031200	1203.4	4968	929	4.728	4.768
73110	1030400	1213.4	5035	939	4.751	4.792
73050	1029600	1225.4	5093	951	4.756	4.797
73090	1029300	1242.5	5200	968	4.791	4.833
73120	1021200	1205.4	4989	931	4.738	4.779
73100	1018700	1231.4	5168	957	4.803	4.845
72990	1016500	1249.5	5277	975	4.826	4.869
73320	1010600	579.40	1479	306	2.929	2.940
73260	1009900	592.42	1533	319	2.967	2.978
73240	1009400	606.45	1590	333	3.005	3.016
73300	1008900	621.48	1646	348	3.038	3.050
73310	1009800	632.48	1690	359	3.065	3.078
73300	1009300	650.52	1766	377	3.114	3.127
73260	1009100	664.55	1870	391	3.226	3.240
73300	1009800	682.56	1941	409	3.262	3.276
73330	1010200	688.59	1971	415	3.285	3.300
73370	1016500	737.66	2190	464	3.410	3.426
73400	1016400	748.60	2279	475	3.497	3.514
73400	1015200	781.74	2433	508	3.576	3.594
73460	1014700	799.75	2511	526	3.610	3.629
73360	1015200	814.79	2606	541	3.673	3.693
73300	1015200	823.80	2651	550	3.692	3.713
73220	1015200	850.84	2831	577	3.813	3.836
73320	1015500	862.85	2875	589	3.824	3.846
73260	1016200	877.89	2964	604	3.871	3.895
73180	1020600	483.25	1089	210	2.582	2.589
73200	1019800	500.28	1148	227	2.629	2.638
73260	1019400	514.31	1190	241	2.654	2.662
73070	1014900	859.85	2896	566	3.853	3.875
72960	1013600	885.88	3034	612	3.911	3.935
72910	1012700	900.92	3113	627	3.944	3.968
73000	1012200	916.94	3184	643	3.987	3.992
72990	1012100	926.96	3247	653	4.002	4.027
73130	1013000	976.03	3545	702	4.157	4.185
73130	1013490	998.08	3681	724	4.221	4.251
73180	1013500	1015.1	3754	741	4.236	4.266
72990	1012300	1248.5	5284	974	4.836	4.879
72980	1011100	1258.5	5352	984	4.858	4.902
73270	1010600	1266.5	5372	992	4.864	4.907
73190	1017000	1262.5	5360	988	4.868	4.912
73190	1017200	1276.5	5482	1002	4.920	4.965

*Discussion of the Results.*

The results given in Tables II and III have been plotted on a large scale in fig. 2. A smooth curve has been drawn through as many of these points as



possible, but leaving out an equal number on either side of the line. Millikan's value of the viscosity has been plotted for room temperatures and the curve extended to these.

For purposes of comparison the results of Barus\* and Fisher† have been included on the same graph. The figures of Barus are calculated from those given in Tables 86 and 89 of his paper in the 'Bulletin U.S. Geological Survey' (1889, No. 54), which is somewhat fuller in detail than that in the 'Annalen der Physik.'‡ These two tables contain, in Barus' opinion, the best results of his work. Owing to an error in the estimation of the bore of the capillary (which led to his obtaining a value of  $\eta$  at 7° C. of 0.000256 instead of the correct 0.000175), it was necessary to recalculate the results to correct for this error. No difficulty was experienced in doing this, as Barus has tabulated the ratio of  $\eta_2/\eta$ , where  $\eta_2$  is the viscosity at some high temperature and  $\eta$  that at a low standard temperature (7° C.). Barus also neglected the value of the slipping coefficient, but he gave sufficient experimental detail to enable this correction to be made.

The recalculated results as compared with those given by Barus are summarised in Table IV.

Table IV.

Temperature, °C.	Barus, $\eta_2 \cdot 10^4$ .	Barus Recalculated, $\eta_2 \cdot 10^4$ .
996	6.693	4.729
994	6.666	4.709
994	6.654	4.700
520	4.977	3.499
562	5.114	3.597
568	5.068	3.648
586	5.210	3.664
598	5.254	3.696
430	4.820	3.386
436	4.865	3.418
446	4.965	3.510
456	4.937	3.469
563	5.351	3.764
568	5.351	3.764
570	5.360	3.771
574	5.364	3.773
976	6.784	4.792
981	6.645	4.694
990	6.842	4.835

It will be seen from the graph (fig. 2) that these points are very irregularly distributed, but the general disposition of the values from 400°-600° C. approxi-

\* *Loc. cit.*

† *Loc. cit.*

‡ *Loc. cit.*



mates to that of the present research. Those near  $1,000^{\circ}$  appear to lie somewhat below the curve. As already mentioned, Barus' work did not claim to be very accurate. The calibration of the bore of the capillary was in error to a considerable amount. The capillary was wound in the form of a helix, of which the coils were touching, the outside diameter of the helix being 0.8 cms. This resulted in a very sharp curvature, with consequent flattening of the capillary. The capillary was heated in the hot gases from various flames. Its temperature was measured by means of thermocouples. It is probably owing to this crude method of heating that most of the irregularities in the results are due, since Barus found that the outside of the spiral was always hotter than the inside, sometimes by more than  $30^{\circ}$  C. Barus took the mean of these temperatures. Another important error is due to the ends of the capillary, which were kept cold by a stream of water. An empirical correction was introduced for this. Also, on account of the gases being collected over running water, appreciable quantities of gas were dissolved and escaped measurement.

The remaining results given by Barus show even greater divergences than those plotted.

It is difficult to draw any conclusions from the work of Fisher, as the eight points shown are the only values for air which have been published by this investigator. Five of these are grouped at about  $500^{\circ}$  C. and lie well on the curve of the present investigation. One of the remaining three points is fairly well on the curve, but the other two show large divergences. Fisher's work throughout appears to have been of a high order of accuracy. The capillary, which was made of Jena 59 III glass, which stood a temperature of  $501^{\circ}$  C. without deteriorating, was calibrated with very great care, due allowance being made for variation in the bore of the capillary. The heating of the capillary was satisfactory, as an electric furnace was employed which Fisher found could be adjusted to remain constant to  $0.1^{\circ}$  C. All pressure measurements were made with mercury monometers which were observed with very accurate cathetometers.

(b) *Theoretical Deductions.*

Sutherland's relation (2) may be expressed as

$$\eta = \frac{kT^{\frac{1}{2}}}{1 + (C/T)} \quad (15)$$

where  $k$  is a constant. Therefore

$$T = \frac{kT^{\frac{1}{2}}}{\eta} - C. \quad (16)$$

If Sutherland's law is true, the curve of  $T$  against  $T^{\frac{1}{2}}/\eta$  should be a straight line, and in this way a very direct test of the law can be made.

From the smooth curve of fig. 2, values of the viscosity were read at intervals of  $50^\circ$  and the term  $T^{1/2}/\eta$  calculated for each of these temperatures. The results are given in Table V.

Table V.

Temperature.		$\eta_s \cdot 10^4$ .	$(T^{1/2}/\eta) \cdot 10^{-7}$ .
$^\circ \text{C.}$	$^\circ \text{Abs.}$		
0	273	1.719	2.624
50	323	1.926	3.014
100	373	2.124	3.392
150	423	2.319	3.752
200	473	2.512	4.095
250	523	2.704	4.423
300	573	2.886	4.753
350	623	3.068	5.068
400	673	3.245	5.380
450	723	3.413	5.696
500	773	3.570	6.020
550	823	3.720	6.347
600	873	3.868	6.669
650	923	4.017	6.981
700	973	4.162	7.292
750	1023	4.301	7.608
800	1073	4.432	7.930
850	1123	4.560	8.253
900	1173	4.688	8.570
950	1223	4.812	8.888
1000	1273	4.933	9.207

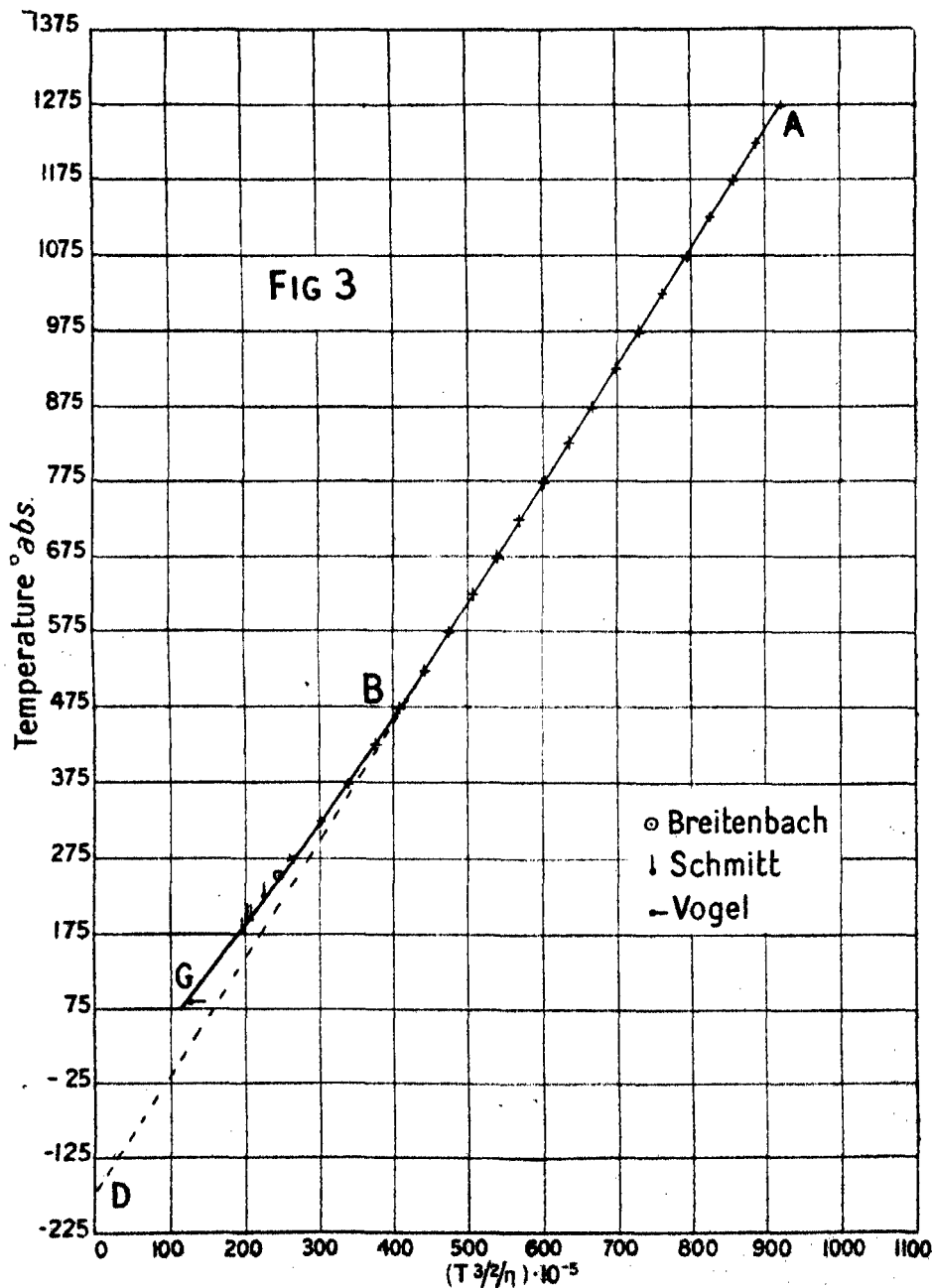
These values of  $T^{1/2}/\eta$  have been plotted against the absolute temperature, in fig. 3, with very striking results. It will be seen that from  $1273^\circ$  abs. to  $573^\circ$  abs. a straight line can be drawn to pass through all the points lying between. Below  $573^\circ$  the concordance is not so good, the values at  $523^\circ$  and  $473^\circ$  lie very slightly above the curve, and as the temperature falls so the deviation becomes more marked.

In order to follow the curve to lower temperatures, the value of  $T^{1/2}/\eta$  has been calculated from the results of observers in this region, as given in Table VI.

Table VI.

Author.	Reference.	$^\circ \text{C.}$	$^\circ \text{Abs.}$	$\eta_s \cdot 10^4$ .	$(T^{1/2}/\eta) \cdot 10^{-7}$ .
Breitenbach	'Ann. d. Phys.,' vol. 67, p. 803 (1899)	-21	252	1639	2.441
Schmitt	'Ann. d. Phys.,' vol. 30, p. 393 (1909)	-50	223	1470	2.265
"	'Ann. d. Phys.,' vol. 30, p. 393 (1909)	-78	195	1280	2.047
"	'Ann. d. Phys.,' vol. 30, p. 393 (1909)	-79	194	1314	2.056
"	'Ann. d. Phys.,' vol. 30, p. 393 (1909)	-96	177	1200	1.962
Vogel	'Ann. d. Phys.,' vol. 43, p. 1235 (1914)	-191	82	579	1.287

These points have been plotted on fig. 3 and lie on a continuation of the curve of the present research, but it is difficult to decide whether the rather marked curvature at B is continued, on account of the irregularity of these



last few points. On the whole, there appears to be slight concavity upwards. Further investigation of this low-temperature region would appear to be very desirable.

It follows from equation (16) that the intercept on the temperature axis of the curve ABG represents the value of the Sutherland constant  $C$ , assuming ABG is straight. The curvature below  $523^{\circ}$  abs. ( $250^{\circ}$  C.) shows, however, that  $C$  is *not* constant below this temperature. The actual value of  $C$  for any particular point on BG is therefore given by the intercept on the  $y$ -axis of the tangent to the curve at this point. It follows that  $C$  increases as the temperature rises, until it reaches a maximum and constant value between  $200^{\circ}$  and  $250^{\circ}$  C., since the curve above this temperature is perfectly straight, and therefore gives a constant intercept on the  $y$ -axis.

It has already been remarked by several investigators that  $C$  tends to rise with temperature. Thus, Bestelmeyer\* investigated nitrogen from  $-190^{\circ}$  to  $300^{\circ}$  C. and found the following values of  $C$  :—

Table VII.

Temperature Range, ° C.	C.
$-190.0$ to $16.4$	103.6
$-78.7$ to $16.5$	110.6
$19.5$ to $98.4$	114.4
$18.4$ to $300.4$	110.3

Vogel† also noticed a similar tendency. His results on several gases can be summarized thus :—

Table VIII.

Gas.	Temperature Range, ° C.	C.
Air .....	$-78.4$ to $0$	104
	$-191.4$ to $0$	99
Nitrogen .....	$-78.4$ to $0$	110.6
	$-191.4$ to $0$	108
Oxygen .....	$-78.4$ to $0$	110.6
	$-191.4$ to $0$	96
Hydrogen .....	$-78.4$ to $0$	56
	$-191.4$ to $0$	30
	$-252.0$ to $0$	32
Helium .....	$-78.4$ to $0$	44
	$-191.4$ to $0$	20
	$-252.0$ to $0$	9

\* 'Ann d. Phys.,' vol. 13, p. 944 (1904).

† 'Ann. d. Phys.,' vol. 43, p. 1235 (1914).

This change of  $C$  has not, however, been clearly recognized before, and this is due to the fact that the values of  $C$  determined for the above temperature range are mean values. The mean value of  $C$  between  $0^\circ$  and  $500^\circ$  C. is obtained from fig. 3 by finding the intercept on the  $y$ -axis of a straight line drawn between these points on the curve, and yields  $C = 121$ . This is in good agreement with Fisher's value  $C = 124$ . The real value of  $C$  at  $500^\circ$  C. is, however, given by the intercept of ABD, which is found graphically on fig. 3 to be equal to 172. Computation by the method of least squares over the range  $573^\circ$  abs. to  $1273^\circ$  abs. gave a value of  $172.6$ , which is in very close agreement with that found graphically.

As the curvature of BG is gradual, a mean value of  $C$  would give comparatively good agreement between theory and experiment over a limited temperature range, and to this is due the considerable success with which Sutherland's formula has appeared to cover such restricted ranges. When extended, however, to large temperature ranges, which has been done almost without exception in the direction of low temperature, the divergence at once becomes apparent (*cf.* Bestelmeyer, Kopsch, Volker, Zimmer, Onnes and Weber, Vogel). Every investigator who has made such a comparison has found the calculated value to fall below the observed. In other words, just such a change appears to take place for all gases in the value of  $C$ , as the curve in fig. 3 leads one to conclude for the case of air.

The agreement between the values calculated by Sutherland's formula in the region where it applies and those observed in the present research is extremely good, as is shown by Table IX. For the computation Sutherland's equation (2) has been employed in the form

$$\frac{\eta_{T_1}}{\eta_{T_2}} = \left(\frac{T_1}{T_2}\right)^{\frac{1}{2}} \frac{1 + (C/T_2)}{1 + (C/T_1)}. \quad (17)$$

All previous experimenters have put  $T_2 = 273^\circ$  abs. and substituted the value of  $\eta$  at this temperature for  $\eta_{T_2}$ . Fig. 3 shows that for air this is erroneous, since at this temperature Sutherland's law is not strictly true. For the calculations in Table IX,  $T_2 = 573^\circ$  abs. was chosen as the standard temperature, and the corresponding viscosity substituted for  $\eta_{T_2}$ . The least-squares value of  $C = 172.6$  was employed. In the second column are given the values of  $\eta_2 \cdot 10^4$  derived from the smoothed curve of fig. 2.

Thus Sutherland's formula represents the change of coefficient of viscosity with temperature between  $200^\circ$  C. and  $1000^\circ$  C. to considerably within the limits of experimental error. It would, therefore, appear reasonable to conclude

Table IX.

Temperature, ° C.	$\eta_s \cdot 10^4$ (observed).	$\eta_s \cdot 10^4$ (calculated).	Difference.
0	1.719	1.587	-0.132
50	1.926	1.837	-0.089
100	2.124	2.071	-0.053
150	2.319	2.291	-0.028
200	2.512	2.500	-0.012
250	2.704	2.697	-0.007
300	2.886	2.886	0
350	3.068	3.066	-0.002
400	3.245	3.239	-0.006
450	3.413	3.406	-0.007
500	3.570	3.566	-0.004
550	3.720	3.721	+0.001
600	3.868	3.871	+0.003
650	4.017	4.016	-0.001
700	4.162	4.157	-0.005
750	4.301	4.294	-0.007
800	4.432	4.429	-0.004
850	4.560	4.558	-0.002
900	4.688	4.685	-0.003
950	4.812	4.809	-0.003
1000	4.933	4.930	-0.003

that the Sutherland model of the molecule has a considerable basis of truth. In this model, the molecules were assumed to be rigid elastic spheres, having a weak attractive field varying inversely as the  $n$ th power of the distance. In other words, the value of  $n$  in Jones's formula is  $\infty$ . This is the same as that employed by Van der Waals in his equation of state, except that the latter definitely assumes an attractive force varying as the fourth power of the distance.

Sutherland denoted by  $C$  the term

$$m^2 f\left(\frac{1}{2a}\right) / c' \quad (18)$$

where  $m$  is the mass of the molecule,  $c'$  a constant, converting kinetic energy temperature into absolute temperature, and  $f(1/2a)$  symbolises the law of potential energy due to the attractive force between the molecules. According to this, there should be a parallelism between  $C$  and the molecular weight of the gas, if the same law of force holds between the molecules of all gases. No direct relation has, however, hitherto been found. Fisher\* thought he detected a relation for nitrogen, oxygen and argon which took the form

$$C = 0.058 M^2 + 74 \quad (19)$$

where  $M$  is the molecular weight. The agreement, however, is very poor and is very probably merely coincidental, since (18) would not lead one to expect an intercept.

\* 'Phys. Rev.', vol. 24, p. 385 (1907).

Apart from the probability that the values of  $C$  at present current are not the maximum constant values, on account of the small temperature ranges so far investigated, it is hardly likely that the law of force between the molecules, and hence  $f(1/2a)$  is the same for all gases.

The deduction of Sutherland's law has been repeated by Chapman\* and Enskog,† using stricter mathematics, but the final formula is the same. Enskog and James‡ have shown that the value of  $C$  is proportional to  $\Delta\phi(\sigma)$  where  $\phi(\sigma)$  is the work required to separate two molecules from contact to infinity, and  $\Delta$  is a pure number depending in value only upon the index of the distance law of the field. In the case of air for low and moderate temperatures,  $C$  has been shown to vary; it follows, therefore, that the index of the distance law of the field must change with temperature, if it be assumed that the conditions still hold under which the relation

$$C \propto \Delta\phi(\sigma)$$

was deduced. This assumption, however, can hardly be justified for low temperatures, because the molecules are then moving more slowly and the mean free path is smaller. The effect of the attractive field around a given molecule in causing deflections of the paths of other molecules near it, without actual collisions, would then become an appreciable factor in viscosity. This effect is neglected in the deduction of Sutherland's law. Collisions between more than two molecules at once would also become of increased importance. Both these factors would make the experimental results higher than those calculated by Sutherland's law, and this is what is found for low temperatures. In other words, the assumptions made in the deduction of the law no longer hold, and it does not necessarily follow that, because  $C$  appears to change with temperature, the index of the distance law of the attractive force is also varying.

In order to obtain further information upon the apparent change in the value of  $C$ , the study is to be extended to other gases. Carbon dioxide is under investigation, and work is shortly being commenced upon argon, which should yield especially interesting results.

#### V. *Summary of Results.*

- (1) The coefficient of viscosity of dry air free from carbon dioxide has been studied by means of the comparative method of transpiration from 15°–1002° C.
- (2) The results show Sutherland's formula for the temperature coefficient of viscosity to hold with great accuracy between 250° and 1000° C.

\* 'Phil. Trans.,' A, vol. 211, p. 432 (1912).

† 'Dissert. Upsala,' 1917.

‡ 'Proc. Camb. Phil. Soc.,' vol. 20, p. 447 (1921).

(3) The value of  $C$ , the Sutherland constant for this range, was found to be 172.6.

(4) Below 250° C. the value of  $C$  falls off as the temperature decreases, and Sutherland's law is no longer true.

In conclusion, the author wishes to thank Prof. J. R. Partington for his kindly interest shown during the course of the work, the Dixon Fund Committee of the London University, and the Chemical Society for defraying most of the expense of the research, and the Department of Scientific and Industrial Research for a maintenance grant which enabled the work to be carried out.

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*The Kinetic Theory of Surface Films.—Part II. Gaseous,  
Expanded and Condensed Films.*

By ROBERT KENWORTHY SCHOFIELD and ERIC KEIGHTLY RIDEAL.

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§ 1. *Introduction.*

The view of Langmuir (1) that the molecules in the films of the insoluble long-chain fatty acids on water, examined by himself and others, are arranged in a single layer and orientated with their carboxyl groups towards the water, is generally accepted at the present time. Arguing chiefly from analogy, he formed the opinion that similar films must exist at the surfaces of aqueous solutions of the short-chain acids, and identified these with the surface excess of solute present in accordance with Gibbs' adsorption equation. In Part I (2) further evidence was obtained which supports this view in cases where the concentration of the solutions is less than 0.1 molar.

Extending a theory due originally to Traube, Langmuir regarded the observed reduction in the surface tension of the water as due in both cases to an outward force exerted by these films, which he considered to be the two-dimensional analogue of fluids respectively in the liquid and gaseous state. He did not undertake a detailed examination of the analogy in either case.

If the analogy between the films of the short-chain acids and gases is a real one, it implies that the outward force  $F$ , which is measured by the difference between the surface tension of the solution and that of pure water, is solely due to the thermal agitation of the molecules in the adsorbed film. In Part I



it was shown that for the fatty acids  $C_4 - C_6$  the variation of  $A$ , the area occupied by a gram molecule in the film (= the reciprocal of  $\Gamma$  calculated from Gibbs' adsorption equation) with  $F$  is completely analogous to that of the volume of a gas with its pressure, provided a surface pressure of 1 dynes/cm. be regarded as comparable with the enormous three-dimensional pressure of (approximately) 50 atmospheres. It was suggested that such slight quantitative discrepancies as were observed can be explained by supposing an alteration in the degree of molecular orientation to occur at small surface pressures. The evidence in the case of these substances was thus seen to be in complete agreement with the kinetic theory of the origin of  $F$ .

The corresponding implication in Langmuir's view of the nature of the films of the long-chain acids is not so clear. On the one hand the successful explanation of the continuity of the gaseous and liquid states of matter, by applying the kinetic theory to the fluid state in general, appears to show that in liquids as well as gases pressure is transmitted by means of direct molecular impacts between free paths; but, on the other, the gradual passage of many liquids into the glassy state as the temperature is reduced, suggests that the molecules are in continual contact. In any case it appears certain that in a liquid (as well as in a gas under very high pressures) a molecule is continually within the range of the *attractive* forces of its immediate neighbours. But it is probable that whereas at temperatures not far below the critical a molecule in a liquid may be regarded as "free," in so far as it is not experiencing a *repulsive* force from more than one of its neighbours at any one instant, as the temperature falls it passes by intermediate stages into a condition in which it is continually in contact with them.

It is evident, therefore, firstly, that the view that the surface tension is reduced by an outward force exerted by these films will be strengthened if it can be shown that the relation between  $F$  and  $A$  corresponds quantitatively with that of a fluid, or that such discrepancies as are found can be satisfactorily explained; and, secondly, that by discovering the precise fluid condition to which each film corresponds some idea can be formed of the manner in which this outward force arises.

## § 2. *The General Form of the $FA/RT - F'$ Curves for Gaseous and Expanded Films.*

In fig. 1 are plotted as ordinate the values of the ratio  $FA/RT$  calculated as in Part I\* from the surface-tension data recently published by Frumkin (3)

\* Except that the solutions being in dilute  $HCl$ , no correction is necessary for electrolytic dissociation.

for solutions of the sparingly soluble acids  $C_8$ ,  $C_{10}$  and  $C_{12}$  in  $n/100$  HCl, while the same ratio calculated from the F—A curves given by Adam (4) for films of the insoluble myristic acid ( $C_{14}$ ) are plotted in fig. 2. We are thus enabled to study the properties of films of a representative series from the readily soluble short-chain acids previously examined to those of their insoluble long-chained homologues.

Since, unlike von Szyszkowski's data for the acids  $C_4$ — $C_6$ , both these refer to a series of temperatures,  $F' = F \cdot T_0/T$  has been used as abscissa in place of F, as by so doing a point on the diagram corresponds to the same value of A irrespective of the temperature. In order to make these figures directly comparable with figs. 3 and 4 of Part I,  $19^\circ \text{C.} = 292^\circ \text{K.}$ , the temperature of von Szyszkowski's measurements, has been used for the reference temperature  $T_0$ . The values found for  $FA/RT$  and  $F'$  from Frumkin's data are given in Table I. Comparing these with the points of fig. 1, it will be seen that there is no variation in the position of the curve for each acid with temperature exceeding experimental uncertainties; hence only one curve is traced for each acid, and regarded as that for the mean temperature.

Table I.

<i>n</i> Caprylic Acid $C_8$		<i>n</i> Caprinic Acid $C_{10}$				<i>n</i> Lauric Acid $C_{12}$					
25° C.		25° C.		5.5° C.		29° C.		18° C.		9.5° C.	
F'	FA/RT	F'	FA/RT	F'	FA/RT	F'	FA/RT	F'	FA/RT	F'	FA/RT
2.1	0.89	0.8	0.73	1.4	0.63	0.5	0.24	0.14	1.00	2.1	0.29
4.1	0.70	2.6	0.54	4.6	0.52	2.4	0.34	0.7	0.19	5.9	0.51
11.0	1.13	7.5	0.74	11.6	1.09	10.2	0.83	2.8	0.31	9.2	0.73
18.6	1.55	14.9	1.24	19.9	1.49	19.8	1.38	7.6	0.66	18.4	1.42
27.0	2.08*	24.7	1.97					16.7	1.23		

$$F' = \frac{0.4343\Delta F}{\Delta \log F} \times \frac{292}{T} \quad FA/RT = \frac{\Delta \log_{10} C}{\Delta \log_{10} F} \text{ (see Part I).}$$

\* Except in this case all values of  $FA/RT$  were calculated between concentrations evidently derived by direct dilution one from another. For this reason the values for lauric acid at  $9.5^\circ \text{C.}$  were not obtained by using the concentrations in the order given by Frumkin.

Comparing figs. 1 and 2 with each other, and with fig. 3 of Part I, it will be seen that the change from the curve of the myristic acid film at  $28^\circ \text{C.}$  to that of lauric acid ( $C_{12}$ ) at  $19^\circ \text{C.}$  marks but a stage in a continuous change of properties, which occurs as we pass from these films through those of the

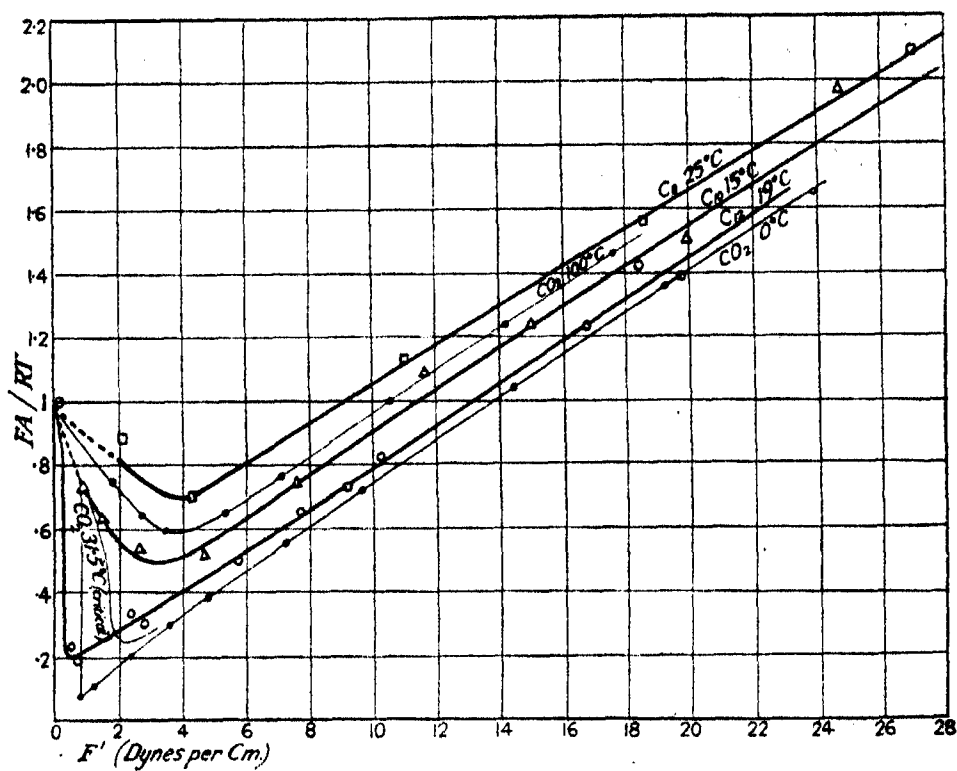


FIG. 1.

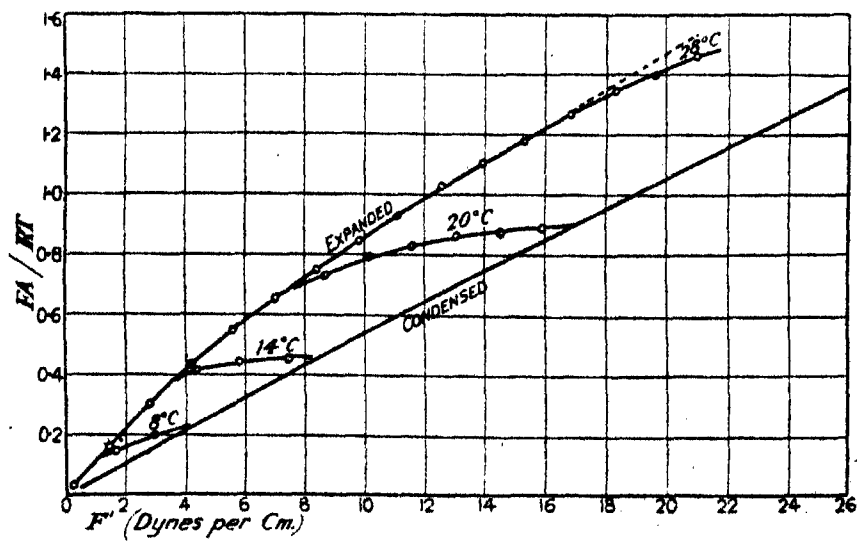


FIG. 2.

intermediate acids to that of butyric ( $C_4$ ). The remarkable resemblance between this series of curves and those connecting  $pv/RT$  and  $p' = p \cdot T_0/T$  for a fluid, first below and then above its critical temperature, is emphasised by plotting on fig. 1 the  $0^\circ \text{C.}$  and  $100^\circ \text{C.}$  isothermals for  $\text{CO}_2$ , together with a portion of that for the critical temperature ( $31.5^\circ \text{C.}$ ) obtained from the data of Amagat (5). Thus, on account of the general resemblance which the  $C_8$  and  $C_{10}$  curves bear to the isothermals of gases, they may conveniently be classed with those of the more soluble acids previously studied under the name "gaseous films"; while the films of the acids  $C_{12}$  and  $C_{14}$  have already been called by Adam "expanded films," and evidently resemble fluids below their critical temperatures. In undertaking a quantitative comparison of the properties of these films with those of fluids, it is convenient to follow the method adopted in Part I, and deal first with the straight portions above 10 dynes/cm., and then with the curved portions below this range. In future a surface pressure above 10 dynes/cm. will be referred to as high, and one below 10 dynes/cm. as low.

### § 3. Gaseous and Expanded Films at High Surface Pressures.

At high surface pressures the curves for the expanded films are straight in all four cases,\* and thus, as in the case of the films studied in Part I, the equation

$$\left. \begin{aligned} \frac{FA}{RT} &= \frac{B}{RT_0} \cdot F' + x \\ \text{or} \quad F(A - B) &= xRT \end{aligned} \right\} \quad (i)$$

is applicable to them. They are also parallel both to each other and to those of the normal acids  $C_4 - C_6$  given in fig. 3 of Part I, showing that the limiting molecular area (24–25 A.U.) is independent of the length of the hydrocarbon chain, and further supporting Langmuir's view that the molecules in these films, when highly compressed, are orientated with their long axes perpendicular to the plane of the interface.

Comparing equation (i) with that of Amagat, which is obeyed by all fluids, liquids and gases, at very high pressures, and which may be written

$$\frac{p''}{RT} = \frac{b}{RT_0} \cdot p' + x,$$

\* The downward bend shown by the  $28^\circ \text{C.}$  curve for myristic acid above 17 dynes/cm. is probably due to the commencement of the transformation to the condensed state, which cannot be followed farther than 21 dynes/cm. owing to collapse of the film.

it will be seen that the isothermals of a fluid when traced on the same diagram as that for a film will be parallel to it if

$$p'/F' = B/b.$$

For the  $\text{CO}_2$  isothermals in fig. 1,  $b$  is taken as 32.5 c.c. per gram molecule.

The value of  $x$  (the intercept of the straight portions of the isothermals on the axis) for a fluid diminishes as the temperature falls, always approaching unity when this is sufficiently high. An examination of Amagat's data shows that for carbon dioxide, ethylene and ether,  $x$  approximates to 0.25 at the critical temperature in each case.\* At  $0^\circ \text{C}$ . ether gives a value as low as 0.04.  $x$  is thus a measure of the relative importance of the disruptive force of thermal agitation and the cohesive force of intramolecular attraction.

The values of  $x$  found for the films of the acids  $\text{C}_8$ ,  $\text{C}_{10}$ , and  $\text{C}_{12}$  are 0.46, 0.35 and 0.23 respectively. These all lie within the range of  $x$ -values shown by fluids, and it is clear that the lateral cohesion in these films increases with the length of the hydrocarbon chain. From Adam's data for the expanded film of myristic acid a value 0.23, identical with that derived from Frumkin's data for lauric acid solutions, is obtained. The almost exact agreement between the high-pressure portion of these two curves is satisfactory, as showing a good first-order agreement between the direct and indirect methods of determining  $A$ ; but, as we should certainly expect  $x$  for  $\text{C}_{14}$  to be less than that for  $\text{C}_{12}$ , it may indicate the existence of a second-order inaccuracy in one of them.

#### § 4. *Gaseous and Expanded Films at Low Surface Pressures.*

It is well known that no one equation has yet been found to express the relation between  $pv/RT$  and  $p$  from 0 to 500 atmospheres as closely as does the equation of Amagat at higher pressures. For this reason it is preferable to make a direct comparison of the curved low-pressure portions of the  $FA/RT - F'$  curves for films, with the directly observed  $pv/RT - p'$  curves for fluids, rather than attempt to trace the analogy between films and fluids by applying to the former the two-dimensional analogue of one of the well-known equations of state.†

\* The curves for fluids are never accurately straight, though a corresponding curvature in the case of films could not be detected with the present data. Strictly, therefore, the value of  $x$  depends on the range of pressures used. Here a range  $p = RT/5$  to  $p = 1.5 RT/b$ , corresponding to a range of  $F$  for fatty acid films of 17–25 dynes/cm., has been used in each case.

† Frumkin (*loc. cit.*) (3) has modified the equation of von Szyszkowski, connecting  $F$  with the concentration of the solution, by introducing a term analogous to the  $a/v^2$  term of Van der Waals' equation. With this relation better agreement between observed and

Table II.

Substance.	$x$	Least value of FA/RT. (Table I.)	Least value of $pv$ /RT for CO <sub>2</sub> .	Temperature CO <sub>2</sub> .
Caprylic acid C <sub>8</sub> .....	0.46	0.70	0.68	° C. 130
Caprinic acid C <sub>10</sub> .....	0.35	0.52	0.45	70
Lauric acid C <sub>12</sub> .....	0.23	0.19	0.21	25

In Table II the least value of FA/RT observed for each film is compared with the least value of  $pv$ /RT for CO<sub>2</sub> at the temperature for which it has the same value of  $x$ . The agreement is much closer than in the similar comparison for the acids C<sub>4</sub>—C<sub>6</sub> (Part I, Table V); and, seeing that the value quoted for C<sub>10</sub> obviously does not correspond to the minimum of the curve, the discrepancies are no greater than the experimental uncertainties. The lower acids were studied in aqueous solution, but for these  $n/100$  HCl was used as solvent, and it should be noted that, while the least values of FA/RT steadily fall from C<sub>4</sub> to C<sub>12</sub>,  $x$  for C<sub>8</sub> (0.46) is *greater* than for C<sub>6</sub> (0.43). Presumably, owing to some action on the carboxyl group, the cohesion in a close-packed film is greater on pure water than on acid. As the area increases the cohesion on water diminishes more rapidly than on acid, so that, when occupying an area large enough to give the minimum value of FA/RT, the acid appears to have much less effect. This is probably because the carboxyl groups have become separated from one another, and the total cohesion is less influenced by their properties.

Because the molecules in these films not only have two distinct parts, but also are presented to one another regularly orientated, the mode of variation of the cohesion with the distance apart may differ from that in a fluid, where molecules meet one another orientated at random. We should not, therefore, expect that the value of  $x$  found for a film at high pressures would be a quantitative indication of its behaviour at low pressures. The agreement noted above for the films on acid may be regarded as a coincidence, or may mean that on dilute acid the carboxyl groups adhere neither at high nor at low pressures, and that, as regards cohesion, the molecules may be regarded as consisting solely of hydrocarbon chains. Presumably on water the carboxyl groups adhere, calculated values of  $F$  is obtained for long-chain acids than with the original equation; but Frumkin is not altogether satisfied with the results. In spite of the fact that the modification was suggested by Langmuir's observations on lateral cohesion between long hydrocarbon chains, and thus rests on a theoretical basis, the foundations of the equation remain empirical and are for this reason unsatisfactory.

especially at high pressures, and so the composite nature of the molecule shows itself.

Considering now the general form of the low-pressure portion to the curves, it will be seen that the  $C_{12}$  curve undoubtedly resembles that of a fluid below its critical temperature, though it is impossible to decide whether the sudden change in  $FA/RT$  occurs at a single "surface vapour pressure" of a little over 0.2 dynes/cm. or takes place over a small range of pressure in this neighbourhood. Below 0.2 dynes/cm. the film appears to obey the relation  $FA = RT$  and so resembles a vapour. Above 0.4 dynes/cm. the film behaves like a liquid, as does also the expanded film of myristic acid, which, however, show no signs of vaporization at the lowest observed pressure (0.3 dynes/cm.). The corresponding portions of the  $C_8$  and  $C_{10}$  curves show that these films resemble gases, and it should be noted that, in the case of  $C_{10}$ , several points have been obtained on the initial falling portion of the curve, proving (what was previously only conjectured from the analogy with gases) that  $FA/RT$  approximates to unity when  $F$  is small. Since we have already noted that fluids at their critical temperatures give a value of  $x$  of 0.25, it is evident that these films on dilute HCl exhibit a general behaviour similar to that of a fluid, at a temperature for which it has the same value of  $x$ .

The exact form of the curves for fluids in the neighbourhood of their critical pressures depends to a large extent on the ratio of the critical volume to the constant  $b$ . This for fluids is usually about 4, and it might be anticipated that as a result of the change from three to two dimensions, the ratio of the critical area to the constant  $B$  for films would be  $4^{2/3}$ .\* But whereas the volume of a molecule is a fixed quantity, the area it occupied at an interface depends on its orientation if it is elongated, and it seems certain that the area occupied by fatty acid molecules will be larger when they are in the act of separating from one another than when close-packed. Hence, the ratio will be increased on this account to an extent which is difficult to estimate, but which will increase with the length of the hydrocarbon chain.

A detailed comparison of the low-pressure portions of the  $C$ ,  $C_{10}$  and  $C_{12}$  curves with the corresponding portions of the 130° C., 70° C., and 25° C. isothermals of  $CO_2$  (with which, having the same value of  $x$ , they coincided at high pressures) shows that while the data for  $C_8$  are insufficient to enable

\* If  $F_{critical} \cdot A_{critical}/RT_{critical} = 0.3$  approx. (Young's rule in two dimensions), the "critical pressure" and thus the "vapour pressure" of a film at room temperature cannot exceed 2 dynes/cm. if  $B = 25 \text{ \AA.U.}$  The considerations advanced below suggest that it will usually be considerably less.

any definite conclusion to be drawn, the initial falling portion of the curve for  $C_{10}$  is undoubtedly to the left of that for  $CO_2$  at  $70^\circ C$ . The leftward displacement of the  $C_{12}$  curve from the  $25^\circ C$ . isothermal is considerable at the lowest  $F$ -values, where the "surface vapour pressure" is about 0.2 instead of 1.5 dynes/cm., and the displacement can still be detected when  $F$  is as large as 5 dynes/cm. For the expanded film of myristic acid this displacement is still more marked, and has the effect of greatly accentuating the negative curvature (which is shown to a lesser degree by the isothermals of liquids, especially just below their critical temperatures). It is evident that this increasing displacement can be readily accounted for on the view that the critical area increases steadily with the length of the hydrocarbon chain.

Broadly speaking, therefore, as was suggested in Part I, the lack of quantitative agreement observed between the curve for a film and one for a fluid, with which it coincides at high pressures, can be attributed to a varying molecular orientation in the film at low surface pressures. In particular, the magnitude of the ratio of  $A$  to  $B$ , of the elasticity, and of the coefficient of expansion of the expanded film of myristic acid at low surface pressures, compared with the corresponding properties for a liquid, which Adam considered to point to the films being in a state analogous to a vapour, can thus be explained, without rejecting the view that this film fundamentally resembles a liquid. It may be suggested that in an expanded film the hydrocarbon chains cling together above the water, but the polar heads are free to exert a lateral bombardment pressure.

#### § 5. Condensed Films.

Below  $6^\circ C$ . the film of myristic acid is in the condensed state, and Adam (6) has shown that the compression curves for the acids  $C_{14}-C_{26}$ , below a temperature which rises with the molecular weight, are indistinguishable from one another. In this condition the films are either "liquid," in which case small talc particles placed on them will move under the influence of air currents, or "solid," showing marked rigidity. Adam\* was unable to detect any definite melting point, and the measurements of Cary and Rideal (7) of the equilibrium pressure of condensed films in equilibrium with crystals reveal no sudden change in entropy. These, together with the fact that the  $FA/RT-F'$  curve for the condensed films resembles the  $pv/RT-p'$  curve for ether at  $0^\circ C$ ., showing a very slight negative curvature at low surface pressures and a straight high-pressure portion for which  $x$  is 0.05, suggest that the film must be compared with a liquid at a much lower temperature than one to which an expanded film is analogous. The slope of the curve gives a limiting molecular area



in the condensed state of 19–20 Å.U. It is possible that, owing to their highly orientated arrangement even at low pressures, we should compare condensed films with liquid crystals, and thus explain the relatively sudden change of properties in passing from the expanded to the condensed state as analogous to crystallisation. But, as the  $p-v$  curves for liquid crystals have not been obtained, no definite conclusions can be drawn. In any case, however, the shape of the transition curve on the  $FA/RT-F$  diagram does not suggest that the change is like the condensation of a vapour, as appeared possible from the  $F-A$  curves of Adam. It is possible that in a condensed film the polar heads, as well as the hydrocarbon chains, are adhering to one another.

#### § 6. *The Mechanism by which the Surface Tension is Reduced.*

A comparison of the relation between  $p$  and  $v$  for fluids and  $F$  and  $A$  for the three types of films—gaseous, expanded, and (liquid) condensed—has shown that for each type there exists a corresponding three-dimensional fluid state. This fact supports in a satisfactory manner the hypothesis that the observed surface tension is the resultant of two forces, one the *unaltered* surface tension of the water (or dilute acid) and the other an outward two-dimensional pressure exerted by the film.

In the case of gaseous and expanded films the outward pressure must be regarded as kinetic in origin, since these films show a behaviour in quantitative correspondence with that of fluids above and only slightly below their critical temperatures respectively. The resistance to compression offered by condensed films which, in their liquid state, are comparable with fluids at temperatures far below critical, or perhaps with liquid crystals, is, on the other hand, probably due more to a steady repulsive force exerted by each molecule upon its neighbours, than to a series of distinct molecular impacts. It appears, therefore, that for liquid as well as solid condensed films the kinetic theory is inapplicable, and  $F$  is equal to the intramolecular thrust integrated over the thickness of the film, i.e., the length of a molecule.

#### *Summary.*

To scrutinize Langmuir's view that surface films of the long-chain fatty acids resemble liquids, and to ascertain the origin of  $F$ , the outward force which they exert,  $FA/RT-F'$  curves for surface films of the sparingly soluble fatty acids  $C_8$ ,  $C_{10}$ , and  $C_{12}$  (as in Part I) have been constructed from the surface-tension concentration data of Frumkin. Those for  $C_8$  and  $C_{10}$  closely resemble the  $pv/RT - p'$  curves for gases at successively lower temperatures

than those to which the films of the more soluble acids  $C_4$ — $C_6$  were previously found analogous. That for  $C_{12}$  is essentially similar to the  $FA/RT - F'$  curve derived from Adam's  $F - A$  curve for the expanded film of the insoluble acid  $C_{14}$ , and both these films resemble liquids just below their critical temperatures, that for  $C_{12}$  showing a surface-vapour pressure of a little over 0.2 dynes/cm.

At high surface pressures the curves are straight and thus obey the relation  $F(A - B) = xRT$  analogous to Amagat's equation for highly compressed gases and liquids.  $B$  has in each case the common value (24–25 Å.U. per molecule) found in Part I for the acids  $C_4$ ,  $C_6$  and  $C_8$ , which further supports Langmuir's view that the molecules in these films under high compression are vertically orientated.  $B$  is still 24–25 Å.U., but  $x$  steadily decreases with the length of the hydrocarbon chain, indicating an increasing lateral cohesion.

At low surface pressure the films show a behaviour corresponding approximately, but not exactly, to that of fluids. This lack of quantitative agreement is attributed to a variation in the molecular orientation which is effective, partly because the molecules in the film have two distinct parts with different cohesions, and partly because their interfacial areas increase as the pressure is reduced. The last factor is considered to account for the expanded film of myristic acid, which is here regarded as liquid, showing properties on account of which it is generally regarded as a surface vapour.

"Liquid" condensed films resemble liquids at much lower temperatures than those to which expanded films are comparable, and should, perhaps, be compared to liquid crystals. It is possible that the carboxyl groups adhere in the condensed but not in the expanded state.

As a result of this detailed comparison with fluids, it is concluded that while the outward force exerted by expanded as well as gaseous films is essentially kinetic in origin, this is probably not true of condensed films.

Our thanks are due to the Board of Scientific and Industrial Research for a grant to one of us (R. K. S.).

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*Some Phenomena Occurring at the Surface of Bubbles in Water.*

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*Introduction.*

Previous work (Alty, 'Roy. Soc. Proc.' vol. 106, p. 315, 1924) indicates that the electrification of gas bubbles depends to some extent on the age of the surface, and on the rate of absorption of the bubble; at the same time it appears that a perfectly new bubble surface in distilled water would be completely uncharged. These effects show that the gas phase at the interface does exert a definite influence on the electrification, and that a definite time must elapse before the latter, which is produced by the liquid phase, attains its equilibrium state. The purer the water, the longer is this charging period.

It is possible that any influence of the gas phase at the surface is masked by the much greater effect of the liquid phase. The most favourable time for the observation of any effects due to the former will, therefore, be during the initial uncharged period immediately after the formation of the bubble. This period is very short, so that measurements of the bubble velocity by a cataphoresis experiment would not be satisfactory, as very few such measurements could be obtained before the surface acquired its full charge. Another method must, therefore, be used to examine the surface during this short interval.

It has been shown by various authors that influences which affect the electrification also affect the surface tension in a similar manner. McTaggart ('Phil. Mag.' vol. 28, p. 367, 1914) worked with solutions of different alcohols, and showed that their relative effect on the electrification was exactly parallel to their effect on the surface tension. Hence an examination of the surface tension of a newly-formed surface should throw light on the surface conditions and on the connection between surface tension and surface electrification.

This is the method adopted in the present work, the surface tension being measured by a modification of the drop weight method. (Iredale, 'Phil. Mag.' vol. 45, p. 1088, 1923). The gas is allowed to rise through the water from a capillary tube and the volume of one bubble is measured in the manner described below. The results obtained indicate that the gas does exert a considerable influence on the surface phenomena until the liquid phase has

had time to reach its equilibrium state, but that, when this latter condition has arisen, the gas has very little effect.

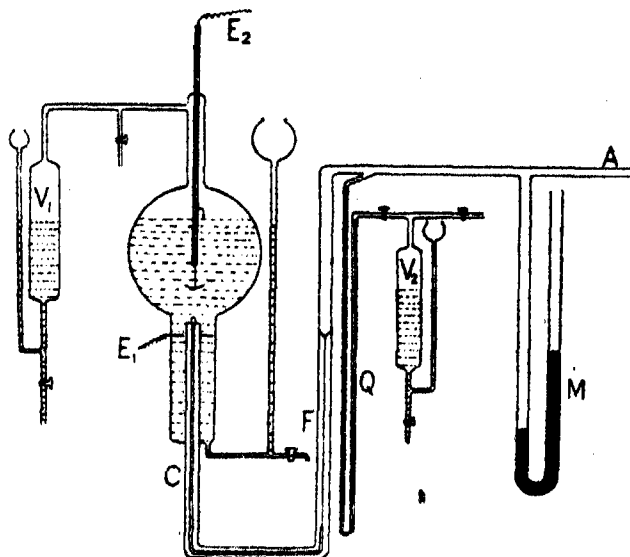


FIG. 1.

*Experimental Arrangements.*

The apparatus is shown diagrammatically in fig. 1. C is the capillary, from the end of which the bubbles are ejected. It is sealed into the glass bulb as shown, and the bubbles rise through the liquid and may be collected in the vessel  $V_1$ . The tip of the capillary C must be carefully prepared if uniform results are to be obtained. This was done in the manner described by Iredale (*loc. cit.*), the tip being first filled with Woods' alloy and then ground and polished thoroughly. The alloy prevents the inner edge of the tube from getting snapped during the grinding. After polishing, the tube is placed in hot water and the alloy melted out. The whole apparatus is thoroughly cleaned with strong chromic acid before use.

The gas to be used enters the apparatus in a pure state at A and passes through the very fine capillary F to the experimental bulb. The relative viscosity of the gas is measured by the time taken to fill the vessel  $V_2$  at atmospheric pressure through the narrow capillary Q. The manometer M gives the pressure inside the apparatus. Consequently, the total volume of gas flowing per second can be calculated.

When the rate of flow was greater than two bubbles per second, it was found

easier to hear them than to see them. Each bubble makes a slight sound as it leaves the capillary, and a microphone placed in contact with the bulb magnifies this sound considerably.

The water used was twice distilled, the second distillation being in silica. If left in the glass apparatus for a considerable period, the conductivity of this water slowly increases, but the change during the course of an experiment is negligible.

In representing the results graphically, the number ( $N$ ) of bubbles emerging per second was plotted against the *total* volume ( $V$ ) of gas flowing per second. The ratio of any ordinate to the corresponding abscissa of this curve will then give the volume of one bubble for that particular value of  $N$ . If the volume  $v$  of one bubble were independent of the number emerging, then the graph obtained would be a straight line. In practice this was found not to be the case, the amount of divergence from the straight line being largely dependent on the nature of the gas used. This method was easier to work, and gave a more continuous set of results than the more direct method of counting the number of bubbles required to fill the vessel  $V_1$ , and hence calculating the volume  $v$  of one bubble. This second method was used in some experiments to check the results of the other method.

It has been pointed out by Harkins ('J. A. C. S.', vol. 41, p. 499, 1919) that in measurements of the surface tension of a liquid by the drop weight method, it is essential that a sufficient interval of time shall elapse between the emergence of successive drops if the true surface tension is to be obtained. He suggests that the surface does not form evenly if the drop formation is too rapid, and that if the liquid moves too quickly, there may be a mechanical effect tending to press more liquid into a drop than would normally be found there. In the case of gas bubbles, the important factor in this connection will be the work done by the gas in displacing the liquid during the formation of the bubble, and Harkins' correction will cause a variation in the bubble volume with the number emerging per second as in the case of liquid drops. Such a variation is found, and is probably explained in the above manner.

This mechanical effect would be expected to be independent of the nature of the gas used, as the density of the latter is negligible compared with that of the liquid. Hence, whatever gas is used, the same  $N$ - $V$  curve should be obtained. At any rate, if the change of density between different gases should cause any small deviations between the corresponding  $N$ - $V$  curves, such deviations would be in the order of the gaseous densities. This is not the case, as will be seen from the results. The different gases do show deviations, which do not appear

to be connected in any way with their densities and are much too great to be due to this cause. For example,  $N_2$  and A, although having different densities, give exactly the same N-V curve, while  $CO_2$  and  $H_2$ , of widely different densities, both give N-V curves deviating greatly, and in the same sense, from that of  $N_2$ , which is taken as standard.

N-V curves obtained in the case of  $N_2$  are shown in figs. 3b and 3c. The amount of curvature varies somewhat from one experiment to another, and is dependent on slight changes in the constitution of the water. In some cases, as in fig. 3b, the curve is practically a straight line. It was found that the  $N_2$  bubbles were always larger than those of the other gases used. Unlike some other gases, the presence of  $N_2$  in the water had no effect on bubbles used in succeeding experiments. This gas was therefore chosen as standard and the other gases compared with it.

In the cataphoresis work already mentioned, it was found that the bubble velocity was independent of the gas forming the bubble except in the case of  $CO_2$ , this gas giving very variable results. It was then suggested that the effect of the  $CO_2$  was due to the solution of the gas in the water with the formation of a layer of carbonic acid round the bubble—i.e., its influence was exerted solely from the liquid side of the interface.

To investigate this point further, the drop weights of air and  $CO_2$  bubbles were compared, the experiment being carried out as follows:—The apparatus was filled with  $CO_2$ -free dry air, and the pressure inside increased until the bubbles emerged at a rate of about 4 per second. The numbers emerging per second were measured as the rate of flow of gas steadily decreased, and the N-V graph was constructed. The air was then replaced by pure  $CO_2$  and the experiment repeated.  $CO_2$  was passed through the water for about two hours and then replaced again by air, when a third experiment was performed. The N-V graphs are shown in fig. 2 (a, b and c). Fig. 2a shows the original air graph. The  $CO_2$  graph (2c) is below this air curve, showing that for any given rate of flow more  $CO_2$  bubbles than air bubbles are formed, so that the volume of each must be less than that of an air bubble. Hence, the surface tension of pure water in contact with  $CO_2$ -free air is greater than that of the same water in contact with  $CO_2$ .

Fig. 2b does not coincide with 2a, although the same water and the same gas are used. In all probability the difference between these two graphs measures the effect of the  $CO_2$  dissolved in the water. This is similar to the effect suggested in the previous paper, viz., that this gas influences the electrification from the liquid side of the surface. On the other hand, the difference

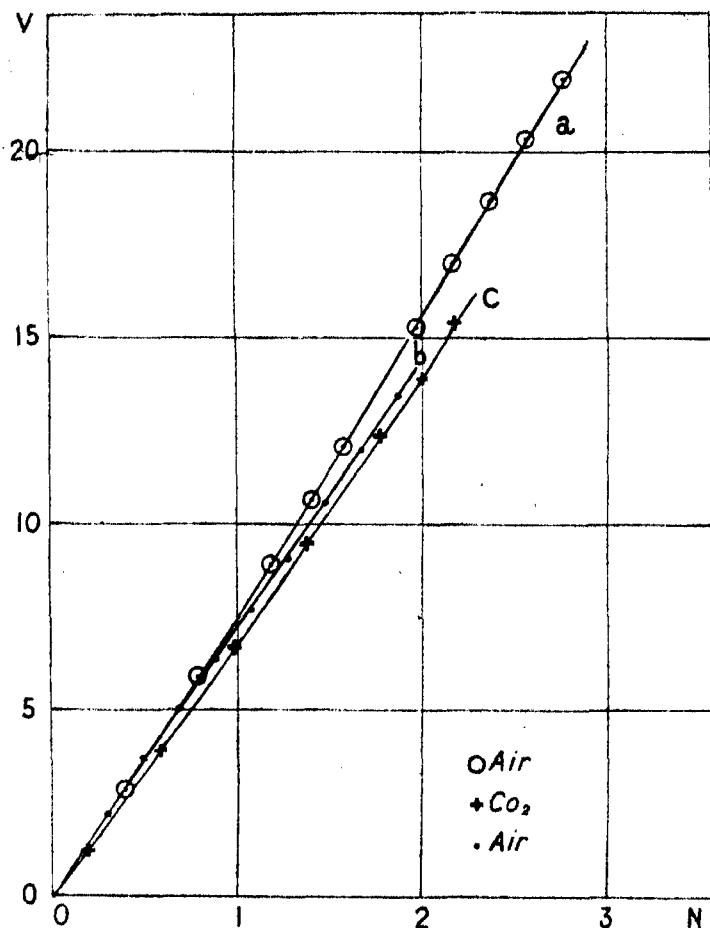


FIG. 2.

between graphs 2c and 2b shows that the  $\text{CO}_2$  gas must influence the surface tension as well as the carbonic acid formed from it later, so that the effect of the  $\text{CO}_2$  may be divided into two distinct parts: first, the part due to the gas acting on the gas side of the interface; secondly, the part due to the gas dissolved in the water and acting from the water side of the surface. Probably its influence on the cataphoretic velocity may be similarly divided.

Combinations of different gases were next compared in the manner described above, a standard gas being used before and after the gas which was to be experimented on. Hydrogen and oxygen were compared in this way, the results being shown in fig. 3a. The points marked + represent the results of the first experiment ( $\text{O}_2$ ) and those marked  $\odot$  the results of the third experiment

( $O_2$ ). It is seen that a new water surface in contact with  $H_2$  has a lower surface tension than a similar surface in contact with  $O_2$ ; also, since the first and third experiments agree exactly, that the presence of  $H_2$  in solution has no influence on the  $O_2$  experiment. When the bubbles emerge more slowly than about one per second, the volumes of  $H_2$  and  $O_2$  bubbles become equal.

Fig. 3*b* shows the results obtained in the same way with  $N_2$  and A. No difference whatever can be detected between these gases.

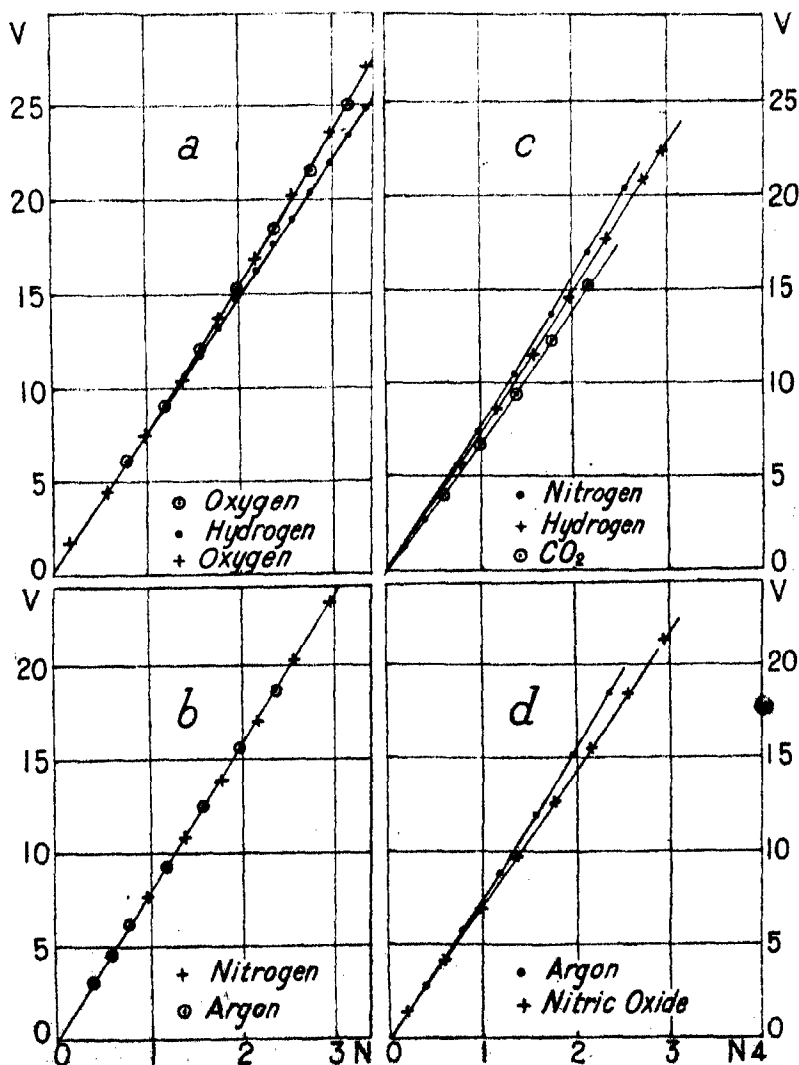


FIG. 3.



The preceding results indicate that neither  $N_2$  nor  $H_2$  in solution in the water influence bubbles used in a succeeding experiment. Hence  $N_2$ ,  $H_2$  and  $CO_2$  may be compared in the same water if they are used in the order named. These gases show considerable differences for rapid rates of flow, the surface tension in contact with  $N_2$  being greatest and that in contact with  $CO_2$  least. Fewer points can be obtained on the  $CO_2$  curve than on the others, because of the very rapid absorption of the gas by the water. These curves are shown in fig. 3c.

Fig. 3d gives similar curves in the case of A and NO. The surface tension is seen to be greater in the case of the former.

Thus, on examination of fig. 3, it is seen that water in contact with  $N_2$ , A and  $O_2$  gives bubbles whose volume is independent of the gas used throughout the whole range of values of N, and that this volume is greater than that obtained when other gases are used. The bubble volumes decrease in the order  $N_2$ , A, and  $O_2$ ,  $H_2$ , NO,  $CO_2$ . It appears, then, that the chemically active gases affect the surface tension, while the inactive ones cause no change. If chemical activity is essential to cause any deviation from the N-V graph given by the more inert gases, then such deviation should be observable on comparing oxygen and ozonized oxygen. This experiment was performed. The ozonization was not very complete, the viscosity of the gas being altered very little during the process. In spite of this, the difference between the two graphs obtained is easily detectable, and is shown in fig. 4. Again, the more active gas gives the smaller bubble volume.

#### *Influence of the Addition of Electrolytes to the Water.*

Some experiments have been carried out on the influence of dissolved electrolytes.  $N_2$  and  $H_2$  were compared in pure conductivity water, which was then replaced by N/100  $H_2SO_4$  and by N/100 KOH in turn, and the experiments repeated in each of the three solutions. As before, a difference was observed between the two gases in pure water. In the acid solution this difference was almost doubled, while in the alkali solution it was increased about threefold. In all three cases the  $N_2$  bubble was larger than the  $H_2$  bubble. This experiment therefore indicates an increase in the effect due to the addition of electrolytes.

#### *Influence of Capillary Diameter.*

During the research two capillaries of diameter 0.0947 cms. and 0.2202 cms. respectively were used. They could be used together, and experiments were carried out using the same water and the same gas supply to test whether

the diameter affected the observed deviations at all. It was found that these deviations between the different gases were larger when the smaller capillary

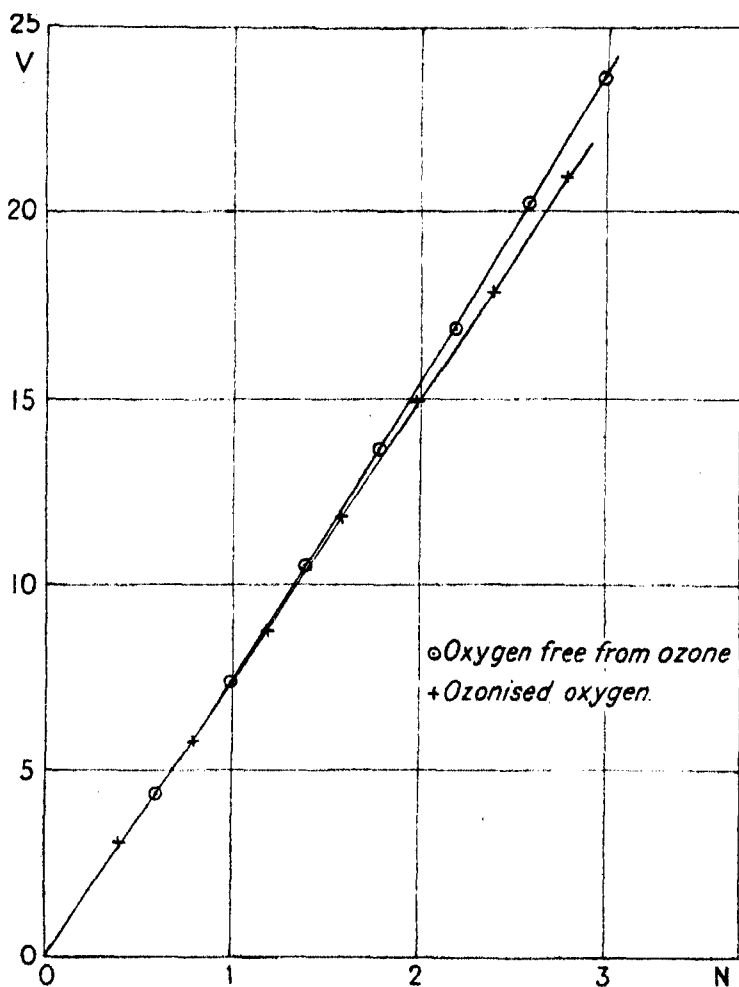


FIG. 4.

was used. One set of results obtained in this way is given in fig. 5. The scale of V for the larger capillary is adjusted so that the two N-V curves for  $N_2$ , as obtained by the two capillaries, coincide. Curve 1 (fig. 5) is then the N-V curve for  $H_2$  as given by the wider capillary, while curve 2 is that for  $H_2$  given by the narrower capillary.

Electrodes  $E_1$  and  $E_2$  were attached to the apparatus as shown in fig. 1, so that a strong field could be applied round the bubble during its formation. If

the electrification of a bubble surface is due to a double electric layer, as described by Helmholtz ('Ann. der Phys.,' vol. 7, p. 337, 1879), this layer will presumably be completed as soon as the surface is formed. If, on the other hand, the electrification is due to adsorption of ions from the liquid—a process which requires some little time to complete—then, during the first few seconds

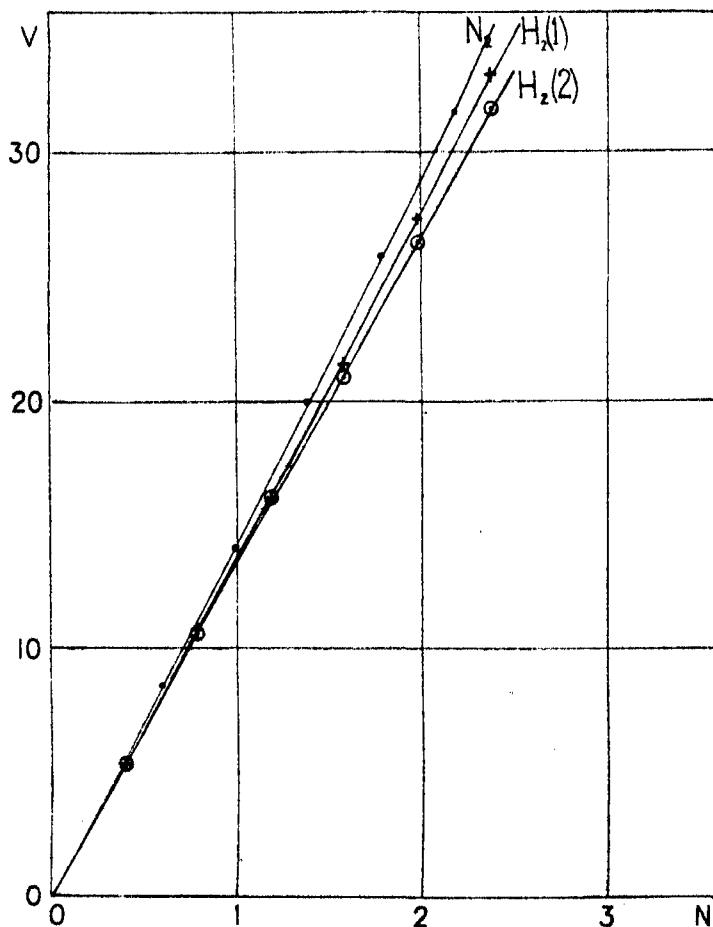


FIG. 5.

after the creation of a new surface, there should be but little sign of electrification on it. The application of the field between the electrodes  $E_1$  and  $E_2$  described above should affect the electrical forces at the bubble surface, and hence, also, the volume of the bubble.

The experiment was tried, the pressure inside the apparatus being kept constant, so that a definite fixed volume,  $V$ , of gas emerged per second. The

number of bubbles formed from this gas was counted (a) with no field applied, (b) with a potential difference of 300 volts/cm. between  $E_1$  and  $E_2$ , (c) with this field reversed. It was found that the application of the field had no effect whatever, the number of bubbles emerging per second being the same in all three experiments for rates of flow between  $N = 4$  bubbles per second and  $N = 0.03$  bubble per second. Evidently the electrification of the surface is inappreciable 30 seconds after its formation. In the cataphoresis experiment, as much as 7 minutes were required for the complete electrification of the surface, so that the two results are not incompatible, and both indicate an adsorption of ions from the liquid as the source of the electrification rather than a *rapidly* formed double layer.

#### *Discussion.*

For the consideration of the above results, it is essential that the mechanical effects of a fairly rapid rate of flow shall be distinguished from any surface effects due to the nature of the gas. As the object of this work is the investigation of the conditions at the interface immediately after its formation, it is necessary that the rates of flow used be not too slow. Consequently, the mechanical effect cannot be entirely avoided, but, as already pointed out, any such force would affect bubbles of all gases equally, causing simply a variation of the bubble volume with the number emerging per second. The actual curve obtained ( $N$ - $V$ ) must be the resultant of this effect, together with any surface phenomena which may take place simultaneously.

That some such phenomena, in addition to the purely mechanical forces considered, must occur is seen on examining fig. 2, where the drop weights of  $\text{CO}_2$  and air are compared. Curves (a) and (b) (fig. 2) are obtained for *air* bubbles entering the *same* water. Hence all mechanical conditions are unaltered, in spite of which the curves do not coincide. On the other hand, no differences whatever are found between argon and nitrogen, which have quite different densities, but are both chemically inert. Owing to this inertness, any surface effect is probably a minimum in the case of these gases, so that the curvature of their  $N$ - $V$  graphs will be chiefly due to mechanical causes. The deviation of the  $N$ - $V$  curves of other gases from those of  $\text{N}_2$  and  $\text{A}$  may, on the other hand, measure the effect of the surface phenomena.

It may be possible to think of such phenomena occurring somewhat as follows:—When the bubble is formed, the surface consists simply of orientated water molecules in equilibrium under their mutual attractions and repulsions (see Adam, 'Nature,' April, 1925, p. 512). As the surface ages, impurities

from the water, and gas from the bubble, will be adsorbed on to the surface until equilibrium is reached. Owing to the greater mobility of the gas, this equilibrium will be attained on the gas side of the interface more quickly than on the liquid side. Suppose that the surface tension of the bubble is greatest at the beginning—i.e., before any adsorption has taken place—and that it falls as the adsorption becomes more complete. Then the tension of a surface of any definite age in contact with a particular gas will depend on the rate of adsorption of that gas. It will fall most rapidly in the case of a readily adsorbed gas, and least rapidly in the case of the gas which is most slowly adsorbed.

Now compare two gases, A and B. Suppose  $N$  bubbles emerge per second. Then the age of the surface when the bubble breaks away will be  $1/N$  seconds. In this time a definite amount of adsorption will have taken place, more in the case of the more adsorbable gas (A) than in that of the other gas (B). Hence the surface tension of the bubble of gas A will have fallen more in  $1/N$  seconds than that of the bubble B. Consequently, the latter will have the larger volume.

As  $N$  decreases  $1/N$  increases, and the surface ages more before the bubble breaks away. The adsorption will therefore be more complete in both gases, so that the difference between the states of the surfaces of the two bubbles will be less than before and their volumes will be more nearly equal. For some value of  $N$ , the more readily adsorbed gas will have saturated the surface before the bubble breaks away, while the surface of bubble B will still be unsaturated. Hence there will still be a difference between the two surfaces. On the other hand, when  $N$  is small enough for the less easily adsorbed gas to saturate the surface, then each bubble of either gas will have a completely saturated surface before it breaks away, and any difference of surface tension due to variations in the completeness of the adsorption will have disappeared. From fig. 3a it is seen that the graphs for  $H_2$  and  $O_2$  coincide for values of  $N$  less than  $N = 1$  per second. Hence the adsorption of  $H_2$  and  $O_2$  must be almost complete within one second of the formation of the surface.

Fig. 3b shows that no differences in the rates of adsorption are visible in the cases of A and  $N_2$  throughout the whole range of values of  $N$ . This must indicate that these two inert gases are adsorbed at approximately equal rates.

In all the cases in which nitrogen was used as the standard with which to compare other gases, it was found that the two graphs obtained did not coincide for the slow rates of flow as in the case of  $H_2$  and  $O_2$  above. This may indicate that the rate of adsorption of nitrogen is too slow to be complete in the times used in this experiment.

If the above explanation of the phenomena is correct, then the rates of adsorption of various gases on to a water surface will be in the following order :—A (slowest),  $N_2$ ,  $O_2$ ,  $O_3$ ,  $H_2$ ,  $NO$ ,  $CO_2$  (fastest).

If the forces of adsorption are considered as being due to the resultant stray fields of the molecules, then the effective forces in the case of the gas bubble will be due partly to the water molecules in the surface and partly to the gas molecules themselves. Any molecule, having adsorbed one other molecule, will have less tendency to hold a second one. Hence, if an electrolyte is added to the water, and therefore adsorbed into the surface, the rate of adsorption from the gas phase should be reduced owing to the smaller attraction of the water molecules. A longer period will then be required before the surface becomes saturated, and the rate of adsorption will depend more on the gas molecule itself. The inactive gases, having little stray field, will then be adsorbed very slowly, while the adsorption of the chemically active gases will not be retarded so greatly owing to their own adsorption forces. Hence, the differences between the gases should, as is the case, be augmented by the addition of electrolytes.

The rate of adsorption will obviously be greater the greater the number of free spaces on the water surface at which adsorption can take place—*i.e.*, the newer the surface. Similarly, the differences between the *rates* of adsorption will be greater the newer the surface.

It has been shown by Harkins (*loc. cit.*) that the ratio (bubble volume/capillary diameter) is not constant, but increases as the diameter decreases. Thus, the smaller capillary forms a relatively larger bubble than the larger capillary, and the rate at which this surface is formed will be greater. Hence the surface will be "cleaner,"—*i.e.*, freer from adsorbed gas, and, therefore, as before the differences between the rates of adsorption of the various gases will be increased. This is supported by the experimental fact that a smaller capillary gives a greater difference between the gases than the wider one.

#### *Summary.*

1. The surface tensions of water in contact with various gases are compared by the drop-weight method. The weight of a bubble is independent of the gas used if the rate of flow is slow enough.
2. To examine a new water surface, the rate of flow is increased until several bubbles emerge per second. After making necessary corrections, it

is found that the volume of the bubble depends on the gas used. It is greater for inert gases and smaller for chemically active gases.

3. When flowing from the same capillary, the gases form bubbles whose volumes can be arranged in decreasing order as follows :— A, N<sub>2</sub>, O<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>, NO, CO<sub>2</sub>.

4. These differences are related to the adsorbability of the gases.

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### *The Line Absorption Spectra of the Alkali Metals.*

By A. L. M. SOWERBY and S. BARRATT, University College, London.

(Communicated by Prof. T. R. Merton, F.R.S.—Received November 10, 1925.)

[PLATE I.]

The line absorption spectra of metallic vapours have become the subject of renewed experiment since the earlier empirical observations have been interpreted in terms of the Bohr theory. Their chief importance now lies in the indication they afford of the character of the normal orbit of the "valency" or "optical" electrons in unexcited atoms, since such atoms can clearly absorb only those series for which this orbit determines the constant term. In this way the normal orbits have already been fixed for several groups of elements in the Periodic Table. The main features of the absorption spectra of the alkali metals were well-known long before the introduction of the Bohr theory. Wood and Bevan and other investigators had found that the principal series of the alkali metals are very readily developed in absorption; so readily that many more of the higher members of these series can be observed in this way than by any emission method. On the other hand, there is no absorption corresponding to the emission lines of the sharp or diffuse series.

These facts together show that the outermost electron in these elements at the temperature used in the observations (200°–500° C.) must be present exclusively in the 1s orbit. Sur and Ghosh ('Phil. Mag.', vol. 49, p. 60 (1925)) have recently found that at much higher temperatures a small proportion of the atoms are capable of absorbing the subordinate series lines, showing that their electrons have been expelled to an outer orbit by thermal excitation.

A further theoretical restriction is placed on the line absorption spectra of the alkali metals by the Selection Principle, according to which in any inter-

orbital transition occurring in absence of an external field the azimuthal quantum numbers of the original and final orbits must differ by unity. The numbers usually assigned to the  $s$ ,  $p$ ,  $d$ ,  $f$ , etc., groups of terms increase by unity from one group to the next, and so the absorption spectrum of the alkalis should be limited to the series  $1s—mp$ , i.e., to the principal series, and such transitions as  $1s—md$  should not occur.

The phenomena of absorption provide a particularly favourable opportunity of testing the Selection Principle in its application to these metals, as there can here be no question of the avoidance of an external field. There is now little doubt that the Principle does not strictly hold. Foote, Mohler and Meggers ('*Phil. Mag.*,' vol. 43, p. 659 (1922)) in experiments upon the excitation of potassium by electron bombardment detected the line  $1s—3d$  (4641 Å) in emission under conditions eliminating, as they considered, any external field adequate to cause a violation of the Selection Principle. The same line and also the second member of the series were observed by Datta in the absorption spectrum of potassium vapour ('*Roy. Soc. Proc.*,' A, vol. 101, p. 539 (1922)), and see also Narayan and Gunnaya ('*Astrophys. Journ.*,' vol. 57, p. 191 (1923)), and it was concluded that this line is developed in the absence of external fields, and contrary to the Selection Principle. An accidental observation of the absorption of the corresponding rubidium line  $1s—3d$  (5165 Å) by the metal vapour led us to enquire whether all the alkali metals are capable of absorbing these "forbidden" lines, and to attempt an approximate estimate of the relative numbers of atoms which at a given moment can absorb the first member of the principal series, and the first member of the combination series  $1s—md$ . We have succeeded in detecting the absorption of the "forbidden" lines in every instance. The results of the further experiments will be given later.

*Absorption of the Line  $1s—3d$  by the Alkali Metals.*

The apparatus was of the type usual in such investigations. The column of absorbing vapour was maintained in an iron tube. The centre of the tube was heated electrically over the length of a foot. The ends were water-cooled and were closed by quartz windows. A carbon arc gave the continuous background, and either a Hilger constant deviation glass spectrograph or a quartz instrument were used according to the position of the line for which search was being made.

*Lithium.*—The metal was volatilised in an atmosphere of argon, and the line  $1s—3d$ , 3196.6 Å., appeared in addition to large numbers of the principal series lines. A band absorption is present in the same region, but the combi-



nation line could safely be picked out by taking a series of photographs at different vapour densities and comparing the intensity changes of the line with those of neighbouring band lines.

*Sodium*.—Argon was introduced into the tube as with lithium. The line  $1s-3d$  lies at 3427 Å, and, again, is in a region of band absorption. It also was selected from among the band lines by its differential behaviour as well as by its wave-length.

*Potassium*.—Reference has already been made to previous observations on the combination lines of this metal. We have observed the line  $1s-3d$  in absorption with atmospheres of argon and of hydrogen and also *in vacuo*. This remark applies also to the corresponding lines of rubidium and caesium.

*Rubidium*.—The metal vapour was obtained by heating a mixture of rubidium chloride and calcium in the furnace tube, and the line  $1s-3d$ , 5165 Å., becomes visually a prominent feature of the absorption spectrum at moderate vapour densities.

*Cæsium*.—The observations on caesium are of especial interest, as the combination series  $1s-md$  had not been previously recorded either in emission or absorption. The vapour was obtained from the chloride of the metal and calcium, and the first two pairs of lines of the new series were photographed. The wave-lengths were determined by comparison with the iron arc standards, measurements being taken on two plates. The wave-lengths found were

	6894.7 Å.
$1s-3d$	6848.5 Å.
	4425.8 Å.
$1s-4d$	4417.7 Å.

The values calculated from the data in Fowler's 'Report on Series Spectra' are 6896.7, 6850.4, and 4426.9, 4418.5 for the same pairs. The observed values are smaller for all four lines by amounts considerably in excess of the possible experimental error, and it may be remarked that the frequency differences between observed and calculated values are almost constant—4.3, 4.3, 5.0, 4.4, if the lines are taken in order of decreasing wave-length.

This suggests that the term values at present accepted for the caesium spectrum are in need of revision. The present measurements are inadequate to give more than an indication of the probable error, as they were made with an instrument of such small dispersion. We have also tried to observe these lines in emission but unsuccessfully. A carbon arc with the poles dipped in caesium

chloride was used as the source of light, but the plates obtained even with long exposures showed no trace of the lines.

*Influence of Foreign Gas Pressure on the Absorption of the Combination Lines.*

We concluded from the foregoing observations that the power of absorbing the combination series  $1s-md$  in a manner not anticipated by the selection Principle is a general property of the alkali metal vapours. The possibility remains, however, that the influence of neighbouring atoms may account for this behaviour, and we have made an attempt to settle this point experimentally for the line 4641 of potassium. Essentially the problem is to determine whether the intensities of the absorption lines in question, produced by a given column of metal vapour, are affected by increase of the gas pressure. Unfortunately no method is yet available for the measurement of intensities of absorption lines, and direct measurements of this type were therefore impossible.

The procedure we have adopted is to determine, both in presence and in absence of a foreign gas, the minimum density of a column of potassium vapour of fixed length which would enable the line 4641 to be photographed in absorption. The metal was introduced in quantity into a glass tube, through which a beam of white light passed into a spectroscope. The tube was gradually heated and the density of the vapour increased until the line 4641 just became photographically visible. We have not attempted to elaborate the method into one of accuracy—for which it is clearly unsuitable—but we have found it suitable for the discussion of this particular point. The experimental details were as follows:—

The ends of a hard-glass tube, 10 inches long and 1 inch diameter, were sealed and blown into thin bulb-shaped ends through which a parallel beam of light could pass without excessive distortion. Two side-tubes were provided through one of which the tube was evacuated, while potassium was introduced through the other after redistillation *in vacuo* from a series of small bulbs. These side-tubes were finally sealed off. A second similar tube was prepared and potassium again introduced, but before sealing, commercial argon was admitted at a pressure just less than atmospheric.

These tubes were placed successively in position along the axis of a resistance furnace of which the ends were closed by glass windows, the temperature of the enclosure being followed by a copper-constantan thermocouple. The light from a 500 c.p. Pointolite lamp was rendered parallel by a collimating lens, and after passing through the furnace was focussed on the slit of a Hilger

constant deviation spectrograph. A series of equal exposures was made on the same plate with the furnace enclosure at progressively higher temperatures, and the negatives so obtained were examined for the first appearance of 4641 as an absorption line against the continuous background. The heating was very slow, the rate being less than  $100^{\circ}$  per hour. With the tube containing potassium *in vacuo* the line appeared at a minimum temperature of  $351^{\circ}\text{C}$ . (vapour pressure of potassium, 1.29 mm.), and with the argon filled tube at  $346^{\circ}\text{C}$ . (vapour pressure of potassium, 1.15 mm.). The temperature step from one exposure to the next was  $10^{\circ}$ , the starting point being the temperature of the cold junction, which was different in the two experiments, and so the appearance temperatures are the same within the limit of experiment. The presence of argon, at a pressure of over two atmospheres under these temperature conditions, had, therefore, no appreciable influence on the absorption of the  $1s-3d$  line by the potassium vapour.

Two main difficulties were encountered in making these measurements. The first arose from the tendency of the metal to deposit on the ends of the tube, which were normally a few degrees cooler than the main portion. This first cut down and finally blocked completely the passage of the light.

Auxiliary heaters were arranged round the ends of the glass tubes, enabling them to be maintained at a temperature above that of the main portion instead of below it, and hindered the deposition of the metal. They also supported the tube axially in the furnace.

The second difficulty was the colouration of the glass by the metal vapour. This became quite rapid above  $300^{\circ}$ , and a new tube had frequently to be prepared for this reason.

#### *Comparison of the Absorption Intensities of the Lines $1s-2p$ and $1s-3d$ .*

It would now seem probable that the absorption of both the principal series  $1s-mp$  and the combination series  $1s-md$  is a normal characteristic of the alkali metal vapours. The lines of the principal series are far more readily absorbed than the others, and it becomes a matter of interest to enquire the relative number of atoms which are able at a given instant to absorb the lines of the two series. So little is known of the mechanism of the absorption of light, that it is difficult in any case to account even for the difference in intensity of absorption of the different members of the principal series. In view of the importance of the phenomenon from the standpoint of the Selection Principle, it is, however, desirable to have some estimate of the

absorption intensity of the combination lines relative to the principal series lines, even if the subject lacks an immediate theoretical interpretation.

As has already been mentioned, no photometric method has yet been developed for line absorption spectra, and in comparing the intensities of the principal and combination lines, we have simply measured the minimum vapour pressures of the metals at which the first line of each series, *i.e.*,  $1s-2p$  and  $1s-3d$ , becomes photographically visible in the same spectrograph under standardised conditions, and have taken the ratio of the two pressures as an indication of the relative intensities of the two lines. By making the assumption that it is possible to detect the absorption of an equal number of quanta of light of different wave-lengths against a continuous background, in the same spectrograph under specified conditions of slit width, &c., it is possible to convert these measurements into an estimate of the relative numbers of atoms able to absorb the various lines. This assumption can, at the best, be only approximately true, and we regard our conclusions from it merely as the first indications obtained upon a somewhat interesting point. The visibility of an absorption line will actually be determined by a large number of factors, *e.g.*, the resolving power of the spectroscope, the purity of the spectrum, the width of the spectrum line, the "contrast" of the photographic plate for the wave-length in question, the exposure (which is particularly troublesome, and is a difficult quantity to fix with any accuracy).

The experiments were of the same nature as those already described, and were carried out with potassium and rubidium. The alkali metal was distilled into a glass tube, argon was admitted at atmospheric pressure and the tube sealed off. Rubidium was prepared by heating the chloride with calcium turnings.

In order to be able to photograph the first member of the principal series which lies in the far red, for both metals, it was found necessary to stain the photographic plates, immediately before use, with dicyanin. The vapour pressures of the metals at which the various absorption lines appeared were calculated from the furnace temperature by the following expressions (for which we are indebted to Mr. A. C. Egerton):—

$$\text{For potassium, } \log p_{\text{mm}} = -\frac{4438}{T} + 7.232.$$

$$\text{For rubidium, } \log p_{\text{mm}} = -\frac{3571}{T} + 6.356.$$

The results are given in the following table :—

Line.	Metal.	Appearance Temp.	Vapour Press.	Ratio.
1s—2p .....	K	° C. 120	mm. $8.7 \times 10^{-5}$	$1.3 \times 10^4$
1s—3d .....	K	346	1.15	
1s—2p .....	Rb	70	$8.8 \times 10^{-5}$	$1.17 \times 10^4$
1s—3d .....	Rb	290	1.03	

Making the above assumption concerning the visibility of the lines in absorption, it would appear that for every atom capable of absorbing the first line of the combination series, there are twelve thousand capable of absorbing the corresponding member of the principal series. The ratio is the same, within the experimental limits, for potassium as for rubidium. The numerical results obtained are of further interest. The absorption of corresponding lines appears at the same vapour pressure for both metals.

This is a conclusion of unexpected simplicity, and we have attempted to test the matter on such lines of the remaining metals as we could observe with the same experimental arrangement.

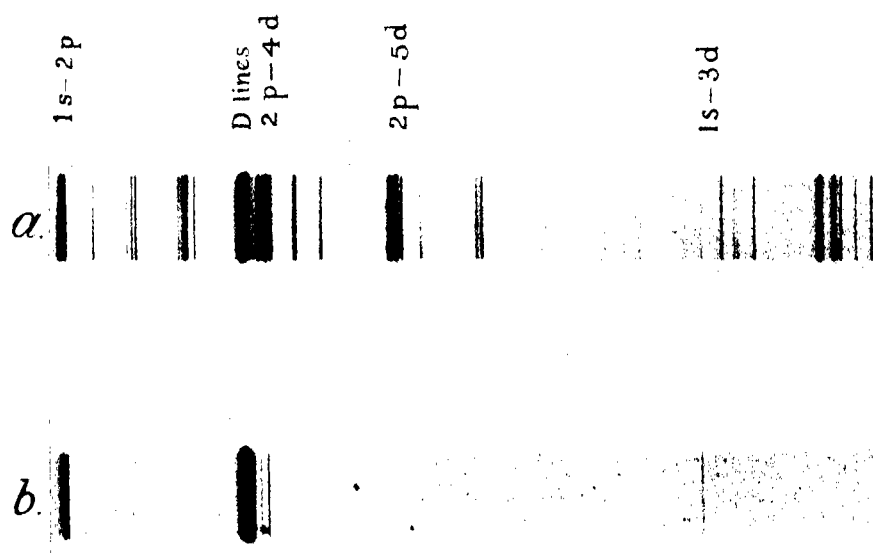
Unfortunately, the first principal line of caesium is outside our wave-length range, and the glass tubes were so rapidly coloured by the metal vapour that we were also unable to find the appearance temperature of 1s—2d for this element. The only remaining lines on which observation was possible were the D lines of sodium. These, under the same conditions as before, could first be detected photographically when the furnace temperature was 190°. Using the vapour-pressure expression

$$\log p_{mm} = -\frac{5420}{T} + 7.566,$$

the corresponding vapour pressure is  $7.2 \times 10^{-5}$  mm., in close agreement with the pressures for potassium and rubidium. The numerical agreement among these results is in fact so close that it must in any case be regarded as accidental, owing to the comparatively large temperature intervals between successive photographs, but it is evident that, within the limits of accuracy of these observations, the absorption of corresponding lines of the different alkali metals examined appear at the same vapour pressure with each metal. This suggests that the mechanism of corresponding absorptions is the same for these metals, not only for the principal series but also for the "forbidden" lines of the







a. Arc spectrum of potassium.

b. Flame spectrum of potassium.





combination series. It would further appear that the phase or condition in which an atom is able to absorb the "forbidden" lines is not excessively rare. We have no estimate at present of the fraction of the total number of atoms able at a given instant to absorb the first line of the principal series. Whatever it may be, it is—for potassium and rubidium—about 12,000 times greater than for the line  $1s-3d$ .

*Emission of the Line  $1s-3d$  in Flames.*

It is to be expected that the bar imposed by the selection principle upon the excitation of certain combination lines will be more rigidly observed in flames than in the arc. We have found that the line  $1s-3d$ , 4641 Å, of potassium is abnormal in this respect also. An intense potassium flame was produced by volatilising the metal in a current of hydrogen and burning the mixture at a jet. The line 4641 was readily photographed and the lines of the diffuse series also appeared. Photographs were also taken of the carbon arc fed with potassium. In the latter source it was expected that the intensity of the line 4641 would have been increased relatively to the lines of the diffuse series,  $2p-md$ . Actually, as may be seen from the reproduction (Plate 1), the opposite effect is observed. We have examined sodium in the same way, but even with long exposures we were unable to photograph the line  $1s-3d$  from the flame.

*Summary.*

(1) The alkali metals are all able to absorb the combination lines  $1s-md$  in the absence of an electric field, contrary to the selection principle.

(2) The first two pairs of the caesium series  $1s-md$  have been observed for the first time, either in emission or absorption. Their wave-lengths indicate that the present accepted term values for caesium are inaccurate.

(3) The absorption of  $1s-2d$  for potassium is not affected by the presence of argon at two atmospheres pressure.

(4) Making certain assumptions, it is estimated that 12,000 times as many atoms are able to absorb the first member of the principal series of potassium and rubidium as can absorb the line  $1s-3d$ , the ratio being the same for the two metals.

(5) The corresponding lines of different alkali metals can be detected in absorption at equal vapour pressures. The atomic "extinction coefficients" must be approximately the same for corresponding lines.

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*Aberrations from the Ideal Gas Laws in Systems of One and Two Components.*

By O. MAASS and J. H. MENNIE.

(Communicated by Prof. A. S. Eve, F.R.S.—Received September 28, 1925.)

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INTRODUCTION.

The principal object of the research described in this paper was a measurement of the deviations from Dalton's Law in gaseous mixtures. Such measurements have been made at low pressures by Maass and Morrison\* and Sivertz† in this laboratory and at high pressures by Masson and Dolley.‡ They worked, however, only at room temperature. It was desired to investigate systems

\* 'Trans. Royal Society of Canada,' vol. xviii, p. 49 (1924).

† *Unpublished.*

‡ 'Roy. Soc. Proc.,' A, vol. 103, p. 524 (1923).

containing water vapour as one component, and this entailed using higher temperatures. An apparatus was devised in which density measurements could be carried out with an accuracy of at least 0.1 per cent. at temperatures up to 200° C. and pressures up to 1 atmosphere, either on a two-component mixture or on a single substance, whether liquid at room temperature or not.

The two-component systems studied were water-carbon dioxide and water-ammonia. As a preliminary to their investigation, it was necessary to determine the density values for the individual components over the desired temperature range. This was done with particular care for water vapour, not only to form a basis for the later measurements, but in the hope of throwing light on the question of the molecular complexity of water in the vapour state, a question which has been the subject of several recent papers.\* In the case of carbon dioxide the density measurements were carried out over the whole range from 200° C. to -70° C., those at the lower temperatures being made with an older apparatus of somewhat different design. These are considered to be accurate to 0.05 per cent., and they have been used to test a new equation of state which the authors have developed.

The subject matter of the paper thus falls naturally into three parts. Part I deals with the experimental determination of the density of carbon dioxide gas from -70° C. to 100° C., and with the equation of state. In Part II the new apparatus is described, the results obtained for the density of water vapour are given, and the question of its association is discussed. Part III includes the measurements on carbon dioxide and on ammonia between 100° C. and 200° C. with the new apparatus, and the results of the investigation of the water-carbon dioxide and water-ammonia systems.

#### PART I.—THE DENSITY OF CARBON DIOXIDE.

##### (a) *Experimental.*

*The Preparation of Carbon Dioxide.*—The carbon dioxide was prepared by dropping pure, dilute sulphuric acid on pure potassium carbonate (Mallinckrodt's). The gas was passed through a water wash bottle to remove any acid spray, and dried by passing over phosphorous pentoxide. By means of a pump with a mercury piston, operated by a water injection pump and automatic control, it was compressed into a tube which was immersed in a mixture of ether and solid carbon dioxide in a Dewar flask. The pump gave a pressure of about one and a half atmospheres, which was sufficient to cause the gas to

\* Kendall: 'Jour. Am. Chem. Soc.,' vol. 42, p. 2477 (1920); Menzies: *ibid.*, vol. 43, p. 851 (1921).

condense slowly at the temperature employed. This method of slow condensation was used in preference to cooling with liquid air, to reduce the possibility of occlusion in the frozen carbon dioxide of any traces of air. The same method had been previously employed in this laboratory for the condensation of acetylene.\*

The receiver was equipped with a "pressure tap,"† opening to the density apparatus. When a sufficient amount of carbon dioxide had been prepared the receiver was immersed in liquid air, the tap opened, and the whole system of tubing thoroughly evacuated by means of an automatic Töpler pump.‡ The carbon dioxide was then allowed to warm up and sublime over into the density apparatus, where it was condensed by means of liquid air in a storage bulb. This bulb was also fitted with a pressure tap, and by keeping it surrounded with ether and solid carbon dioxide in a Dewar flask the carbon dioxide which it contained could be stored indefinitely. By opening the tap carbon dioxide could be admitted in small amounts, as required, to the rest of the system.

*Apparatus and Procedure.*—The method employed in measuring the density was a modification of that described by Maass and Russell.§ It had already been used in the determination of the densities of several organic compounds,|| so that a detailed description should be unnecessary.

Essentially it consists of observing the pressure of the gas contained in a known volume, maintained at a known temperature; condensing the gas by means of liquid air into a small glass bulb strong enough to withstand considerable pressure, sealing off the bulb and weighing it after it has reached room temperature. The bulb is again cooled in liquid air, the tip is broken off, care being taken to lose none of the glass, and the bulb is finally weighed empty.

This method possesses the advantage over other methods of obtaining gas density by direct weighing, that the weight of the container is of the same order as the weight of its contents, and a comparatively large volume of gas can be weighed on an ordinary analytical balance.

The known volume consisted of a glass globe of about one litre capacity, fitted with a tap and contained in a bath. The tap was protected from splashing

\* O. Maass and E. H. Boomer, *unpublished*.

† O. Maass and D. M. Morrison: 'Jour. Am. Chem. Soc.,' vol. 45, p. 1677 (1923).

‡ O. Maass: 'Jour. Am. Chem. Soc.,' vol. 41, p. 53 (1919).

§ 'Jour. Am. Chem. Soc.,' vol. 40, p. 1847 (1918).

|| O. Maass and E. H. Boomer, *unpublished*.

of the bath liquid, and was encircled by a coil of glass tubing through which hot water could be circulated when the bath was at a very low temperature or cold water when the bath was hot, to prevent sticking or melting of the tap grease. The volume of the globe had been determined by weighing it filled with distilled water, and a graph had been prepared showing the variation of volume with temperature calculated from the expansion coefficient of glass. At the close of the experiments the globe was removed and its volume re-determined, the previous value being confirmed within 0.01 per cent.

The bath consisted of a five-litre Pyrex beaker, supported on corks in an outer vessel and lagged with wool. Measurements were made at  $-70^{\circ}$ ,  $-50^{\circ}$ ,  $-25^{\circ}$ ,  $0^{\circ}$ ,  $20^{\circ}$ ,  $50^{\circ}$  and  $100^{\circ}$  C. At the lowest temperatures the bath liquid consisted of ether, cooled by the addition of solid carbon dioxide. It was stirred by a small motor-driven stirrer, and the temperature hand regulated by the addition of small lumps of carbon dioxide. At  $0^{\circ}$  C. a strong brine solution was used, cooled with ice and hand regulated by adding small lumps of ice. For the higher temperatures water was used, the temperature being maintained at  $20^{\circ}$  by adding hot or cold water as required, at  $50^{\circ}$  by means of a small carbon filament lamp immersed in the bath, and at  $100^{\circ}$  by passing in steam. It was found quite possible to keep the temperature constant within  $0.1^{\circ}$  during the time necessary to take a reading of the pressure.

Temperatures were read at  $-70^{\circ}$  and  $-50^{\circ}$  on a Leeds and Northrup platinum resistance thermometer which had been calibrated by the United States Bureau of Standards. The ordinary Wheatstone Bridge method was used to measure the resistance of the thermometer. Two carefully balanced, 25-ohm resistances were employed, with a variable resistance consisting of a Leeds and Northrup box of the plug type reading to 0.1 ohm, in conjunction with the platinum wire resistance described by Maass and Wright.\* The latter could be read to 0.001 ohm, corresponding to  $0.01^{\circ}$ . The ice point of the thermometer was determined from time to time and found to remain perfectly constant. The values of  $F$ , the fundamental interval, and  $\delta$ , the constant of the Callendar-Barnes formula, were taken from the Bureau of Standards certificate. At the other temperatures mercury thermometers were used, which were checked at each point against the platinum thermometer.

Pressures were read on a manometer with a scale graduated in millimetres and etched on a mirror. It could be read to 0.1 mm. A mercury reservoir, to which suction or pressure could be applied, permitted adjustment of the mercury level in the manometer. The mercury on the side connected to the apparatus

\* 'Jour. Am. Chem. Soc.,' vol. 43, p. 1170 (1921).

was always brought up just to touch a glass point sealed into the manometer tube, so that a single scale reading gave the pressure.

The procedure was as follows:—The volume with all connecting tubing was first evacuated by means of the automatic Töpler pump, swept out with carbon dioxide and re-evacuated several times. Carbon dioxide was then admitted by opening the tap on the storage bulb to approximately the desired pressure. The pressure could be observed on a second, rough manometer connected to the system. The bath, which had meanwhile been brought to the desired temperature, was carefully regulated and the pressure was read on the manometer. The tap on the volume was then closed and the connecting tubing evacuated. Sealed on to a series of side tubes were several glass bulbs with thick walls and long, constricted, capillary necks. One of these was immersed in liquid air, the tap leading to the pump and storage bulb was closed, and the tap on the volume opened. The carbon dioxide condensed in the small bulb, which was then sealed off at the constriction. A small residual pressure was always observed. This was subtracted from the original pressure, but an additional correction had also to be applied for the uncondensed gas in the "dead space" between the tap on the volume, the tap leading to pump and storage bulb, and the mercury level in the manometer. It was to keep the volume of this dead space constant that the mercury level in the manometer was always brought to the same point before a reading was made. The volume of the dead space had been determined when the apparatus was built. As the residual pressure was very small, usually less than 2 mm., the mass of gas in the dead space could be calculated with sufficient accuracy from the simple gas equation,  $pv = m/MRT$ . The amount found was added to that determined by weighing the bulb.

The bulb was allowed to warm up to room temperature before weighing. Several explosions occurred, due to faulty glass, one of which actually took place in the balance case. Thereafter, although some special glass tubing, free from seams and flaws, had been obtained for the making of bulbs, the precaution was observed of cooling the room in which the weighing was done by opening the windows. As this work was carried out during the winter, the temperature at which the bulbs were weighed could be brought ten or fifteen degrees below the maximum to which they had been warmed. The weighing was done with a calibrated set of weights, against which those used in determining the volume had also been calibrated.

After weighing, the bulb was cooled again in liquid air; a nick was made in the neck with a sharp file and the tip broken off over a sheet of glazed paper

to avoid any loss of fragments of glass. The carbon dioxide was allowed to evaporate, the bulb was dried in the oven, air being sucked through by introducing a fine capillary tube connected to a water pump. The empty bulb was then weighed, along with the broken tip. Finally, it was filled with distilled water and weighed again to obtain the volume, in order to correct for the air contained in it during the second weighing.

Weighings were made to 0.0001 gm. The probable error in the weight is about 2 in 5000 at the lowest pressures used and, at the highest pressures, not over 2 in 20,000. The probable error in the pressure readings is not over 1 in 7000 at the highest pressures. Temperatures were read to 0.1°, the probable error being thus from 1 in 2000 at the lowest to 1 in 3000 at the highest temperatures. The accuracy of the measurements thus depends on the accuracy of the temperature readings, and may be taken as better than 1 in 2000, or 0.05 per cent.

*Results.*—The results obtained are shown in Table I. The last column contains the “apparent molecular weight,”  $M'$ , calculated from the equation,  $pv = m/M'RT$ . This is the molecular weight of the ideal gas which would satisfy the pressure volume and temperature conditions experimentally observed. A specimen calculation follows :—

Temperature of bath	..	..	..	19.7° C.	292.79° K.
Temperature of room	..	..	..	25.5° C.	298.5° K.
Initial pressure	..	..	..	729.1 mm.	
Correction for room temperature	..			3.4	
				<hr/>	
				725.7	

Residual pressure	..	..	..	1.8	
				<hr/>	
Net pressure	..	..	..	723.9 mm.	
Volume of dead space	..	..	..	43.2 c.c.	

Weight of residual gas in dead space ..  $m = M \frac{pv}{RT}$

$$m = \frac{44.0 \times (1.8/760) \times 0.0432}{0.082 \times 298.5} = 0.0002 \text{ gm.}$$

Weight of bulb filled with water	..	..	..	19.29 gm.	
Weight of bulb empty	..	..	..	13.46	
				<hr/>	
Volume of bulb	..	..	..	5.83	



Weight of bulb and carbon dioxide .. 15.5085 gm.  
 Weight of bulb empty .. .. 13.4607

---

2.0478

Correction for air in empty bulb .. 0.0070

Weight of carbon dioxide in dead space . 0.0002

---

Total weight of carbon dioxide .. .. 2.0550 gm.

$$M' = m \frac{RT}{pv} = \frac{2.0550 \times 0.08209 \times 29279}{(723.9/760) \times 1.1715} = 44.260.$$

In fig. 1 the values of  $M'$  are shown plotted against pressure. It will be seen that they give a series of straight lines which pass through the theoretical molecular weight at zero pressure.

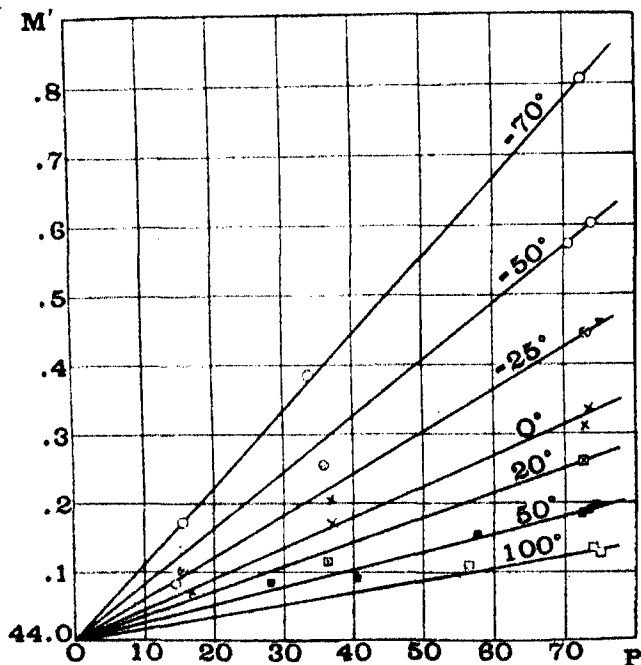


FIG. 1.

In fig. 2 the values of  $M'$  at 760 mm. are shown plotted against temperature. The points marked with a circle were read off from the isothermals of fig. 1, while those marked with a cross were obtained as described later in Part III. From this curve the value of  $M'$  at 1 atmosphere for any temperature within the limits of the experimental work may be read. The density in grams per

Table I.

Temperature.	Pressure.	Weight.	Volume.	M'.
°C.	mm.	gm.	c.c.	
- 70.2	725.4	3.0032	1169.43	44.804
	341.8	1.4015		44.383
	157.0	0.6407		44.171
- 50.3	739.0	2.7741	1169.89	44.601
	705.9	2.6470		44.571
	147.4	0.5467		44.085
- 24.9	731.6	2.4578	1170.44	44.444
	358.9	1.2006		44.255
	158.5	0.5277		44.100
0.1	735.5	2.2414	1171.04	44.336
	729.2	2.2201		44.311
	371.0	1.1255		44.170
	368.4	1.1185		44.205
	167.7	0.5076		44.070
19.7	723.9	2.0550	1171.50	44.280
	361.5	1.0229		44.117
50.3	742.6	1.9068	1172.19	44.196
	735.5	1.8881		44.189
	725.7	1.8630		44.185
	577.2	1.4805		44.152
	405.7	1.0393		44.092
	283.4	0.7258		44.085
99.9	743.0	1.6534	1173.34	44.133
	748.5	1.6794	1173.26	44.130
	563.1	1.2628		44.107

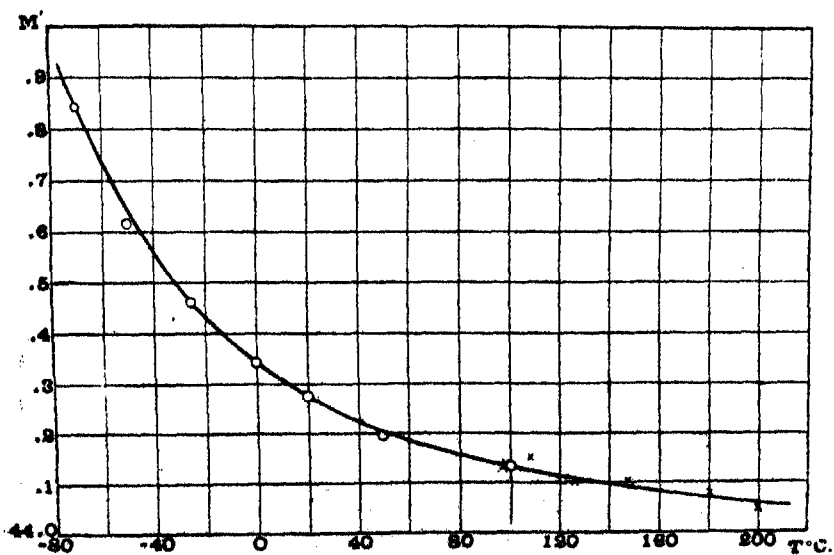


FIG. 2.

litre is then given by  $d = M'/RT$ , and the volume of one gram molecule by

$$V = \frac{44}{M'} RT.$$

The curve has been extrapolated to  $-78.5^\circ \text{C.}$ , the temperature at which the gas condenses to the solid. Using the density value so obtained in the Clausius-Clapeyron equation, the latent heat of sublimation is calculated to be 137.7 calories per gram, in good agreement with that found experimentally by W. H. Barnes,\* namely, 136.9 calories per gram.

(b) *Theoretical.*

*The Variation of Van Der Waals' "b."*—The most important of the corrections to be made to the simple gas equation,  $pv = RT$ , are, of course, those due to the effects of molecular attraction and molecular volume, symbolized by the constants " $a$ " and " $b$ " in the familiar equation of van der Waals. Most of the later equations of state have the advantage of representing more accurately than does that of van der Waals, the results of experiment, but this added exactness has been gained by the addition of further empirical or semi-empirical constants. Van der Waals' equation, though only a first order approximation, brings out most clearly the effect of molecular attraction and of molecular volume.

A consideration of the assumptions made by van der Waals shows why his equation is inadequate to represent successfully the results of experiment. In the first place, " $a$ " is assumed to be independent of temperature. This is probably not the case, since, at higher temperatures, the violence of the impact on collision between the molecules might be expected to cause a deformation of the molecular structure which would alter the external field surrounding the molecule. Furthermore, Richards† has shown that " $b$ ," which is proportional to the actual volume of the molecules, cannot be regarded as constant, and that at higher pressures and temperatures the molecules themselves may actually be compressed.

These effects are to be anticipated only at high pressure and temperature. It is the object of the present discussion to show that, even under more ordinary conditions " $b$ " is not constant, but can be expressed as a function of the temperature. Incidentally, the equation is stated in a new form, and it is demonstrated that the original relation, deduced by van der Waals, can be obtained by starting from quite a different viewpoint.‡

\* O. Maass and W. H. Barnes, *unpublished*.

† 'Jour. Am. Chem. Soc.,' vol. 36, p. 2417 (1914).

‡ Cf. Taylor: 'Treatise on Physical Chemistry,' vol. 1, p. 98 (1924).

Instead of regarding, as van der Waals did, the effect of molecular volume on the total volume occupied by the gas, its effect on the pressure registered by a manometer is considered. It is assumed for the moment that the molecular attraction can be neglected. The molecules which strike the manometer do not travel from the midst of the bulk of the gas, but come from a distance,  $l$ , where  $l$  is the mean free path. Consider a manometer surface 1 square centimetre in area, which is in contact with a gas of volume,  $V$ , and let  $N$  represent the total number of molecules and  $n$  the number of molecules per cubic centimetre. Let  $x$  be the velocity of the molecules. Then the number of impacts made per second by one molecule will be  $\frac{1}{2} (x/l)$ , the expression  $x/l$  being halved because only the impacts on the manometer and not those at the other end of the path are here considered. The number of molecules concerned will be  $\frac{1}{3}n (2r + l)$ , where  $r$  is the radius of the molecule,  $(2r + l)$  being the distance from which the molecules can reach the manometer, and the numerical factor,  $\frac{1}{3}$ , signifying the number which, on the average, move perpendicular to the manometer surface. Each impact produces a pressure  $2mx$ , so that the pressure,  $p$ , per square centimetre is

$$p = 2mx \cdot \frac{1}{3}n (2r + l) \left( \frac{1}{2} \cdot \frac{x}{l} \right) \quad \text{or} \quad p = \frac{1}{3}mnx^2 \left( 1 + \frac{2r}{l} \right). \quad (1)$$

Since  $l$  is large compared to  $r$ , this may be written

$$p \left( 1 - \frac{2r}{l} \right) = \frac{1}{3}mnx^2,$$

because

$$\left( 1 + \frac{2r}{l} \right)^{-1} = 1 - \frac{2r}{l}.$$

From the definition of  $N$  and  $n$ , it follows that  $n = N/V$ . Hence,

$$pV \left( 1 - \frac{2r}{l} \right) = \frac{1}{3}mNx^2 = RT,$$

where  $V$  contains one gram molecule. But  $l$ , the mean free path, is equal to

$$\frac{1}{4\sqrt{2}\pi r^2 n} = \frac{1}{4\sqrt{2}\pi r^2} \cdot \frac{V}{N}.$$

Hence,

$$pV \left( 1 - \frac{8\sqrt{2}\pi r^2 N}{V} \right) = RT,$$

or

$$p (V - 8\sqrt{2}\pi r^2 N) = RT.$$

Introducing the correction for molecular attraction and putting  $8\sqrt{2\pi r^3 N}$  equal to " $b$ ," we have an equation identical with that of van der Waals :

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT, \quad (2)$$

and " $b$ " is proportional to the actual volume of the molecules,  $4/3\pi r^3 N$ .

If the approximation used in the above derivation is not made the result is somewhat different in form. Going back to equation (1)

$$\begin{aligned} p &= \frac{1}{3}mnx^2\left(1 + \frac{2r}{l}\right) \\ &= \frac{1}{3}m \frac{N}{V} x^2\left(1 + \frac{2r}{l}\right) \\ &= \frac{RT}{V}\left(1 + \frac{2r}{l}\right) \\ &= \frac{RT}{V}\left(1 + 8\sqrt{2\pi r^3} \frac{N}{V}\right) \\ &= \frac{RT}{V^2}(V + 8\sqrt{2\pi r^3}N). \end{aligned}$$

Finally,

$$\left(p + \frac{a}{V^2}\right) = \frac{RT}{V^2}(V + b)$$

$$pV^2 + a = RT(V + b),$$

or

$$pV^2 - RTV + a - RTb = 0. \quad (3)$$

The above is, however, based on the assumption of a mean free path which is independent of molecular forces. This assumption is incorrect for the reason, perhaps most clearly and concisely stated in the words of Sutherland\* : "Molecular attraction has been proved to exist, and though negligible at the average distance apart of molecules in a gas, it is not negligible when two molecules are passing quite close to one another ; it can cause two molecules to collide which, in its absence, might have passed one another without collision, and the lower the velocities of the molecules the more effective does molecular force become in bringing about collisions which would be avoided in its absence."

The numerical value of the mean free path is calculated from viscosity measurements by means of the formula—

$$\eta = \frac{1}{3}\rho xl,$$

where  $\eta$  is the coefficient of viscosity,  $\rho$  the density,  $x$  the velocity of the

\* 'Phil. Mag.' ser. v, vol. 36, p. 507 (1893).

molecules, and  $l$  the mean free path. If  $l$  were independent of temperature,  $lp$  would be constant and  $\eta$  would vary as  $x$ , i.e., as  $\sqrt{T}$ . Actually,  $\eta$  is found to vary with temperature more rapidly than is required by the above relationship. Now Sutherland\* has derived a formula for the variation of viscosity with temperature :—

$$\frac{\eta}{\eta_0} = \left(\frac{T}{273}\right)^{\frac{1}{2}} \left( \frac{1 + \frac{c}{273}}{1 + \frac{c}{T}} \right),$$

where  $\eta_0$  is the viscosity at 0° C. and  $c$  is a constant. This gives, for the relationship of mean free path to temperature,

$$\frac{l}{l_0} = \frac{1 + \frac{c}{273}}{1 + \frac{c}{T}}$$

where  $l_0$  is the mean free path at 0° C. Therefore,

$$l = \frac{1}{4\sqrt{2}\pi r^2 n} \cdot \frac{1 + \frac{c}{273}}{1 + \frac{c}{T}} \quad \text{if} \quad l_0 = \frac{1}{4\sqrt{2}\pi r^2 n}.$$

Introducing this into the foregoing derivation, we get

$$b = 8\sqrt{2}\pi r^3 N \frac{1 + \frac{c}{T}}{1 + \frac{c}{273}},$$

or, putting

$$\frac{8\sqrt{2}\pi r^3 N}{1 + \frac{c}{273}} = \beta, \quad b = \beta \left(1 + \frac{c}{T}\right). \quad (4)$$

Equation (2) then becomes

$$\left(p + \frac{a}{V^2}\right) \left\{V - \beta \left(1 + \frac{c}{T}\right)\right\} = RT, \quad (2A)$$

and equation (3) becomes

$$pV^2 - RTV + a - RT\beta \left(1 + \frac{c}{T}\right) = 0. \quad (3A)$$

This is the equation which has been applied to the experimental data.

\* *Loc. cit.*

For a constant temperature equation (3A) reduces to equation (3). Substituting in the latter

$$V = \frac{M}{M'} \cdot \frac{RT}{P},$$

where  $M$  is the theoretical and  $M'$  the "apparent" molecular weight, and expressing  $M'$  as a power series in terms of  $p$ , there is obtained

$$\frac{M'}{M} = 1 + \left( \frac{a - RTb}{R^2 T^2} \right) p + 2 \left( \frac{a - RTb}{R^2 T^2} \right)^2 p^2 + \dots * \quad (5)$$

The coefficient of  $p^2$  is very small, so that, to a first approximation,

$$\frac{M'}{M} = 1 + Ap. \quad (5A)$$

This, which is the equation of a straight line, is the general equation of the isotherms of fig. 1.

It is to be emphasised that the applicability of equations (2A) and (3A) is restricted to the range of pressure and temperature for which the mean free path equation is valid. Their significant feature lies in the direct linking up of gas densities with the results of mean free path measurements.

*Discussion of Results.*—The value of  $r$  for carbon dioxide, calculated by Jeans† from Breitenbach's‡ determination of the viscosity at 0° C., is  $2.31 \times 10^{-8}$  cm. Sutherland§ estimated the value of "c" for carbon dioxide to be 277. Introducing these figures into equation (4), we get—

$$\beta = 0.132 \quad \text{and} \quad b = 0.266.$$

Now, introducing this value of "b" into equation (3), and using the experimental values for  $p$ ,  $V$  and  $T$  at 0° C., we get  $a = 9.79$ . Using this value of "a" and the values of  $V$  given in column 2 of Table III, "b" is then found from equation (3) for each temperature. The figures so obtained are shown in column 2 of Table II, while the third column of the same table gives the values of "b" calculated from equation (4). The data of Table II are represented graphically in fig. 3.

It will be seen that "b" displays the expected regular variation with temperature. The agreement between theoretical and experimental values is reasonably good, except at the lowest temperature. This discrepancy is, however,

\* We are indebted for the mathematical work involved in obtaining this series from equation (3) to Mr. M. Home.

† 'Dynamical Theory of Gases,' p. 288 (1921).

‡ 'Ann. der Physik,' vol. 5, p. 166 (1901).

§ *Loc. cit.*

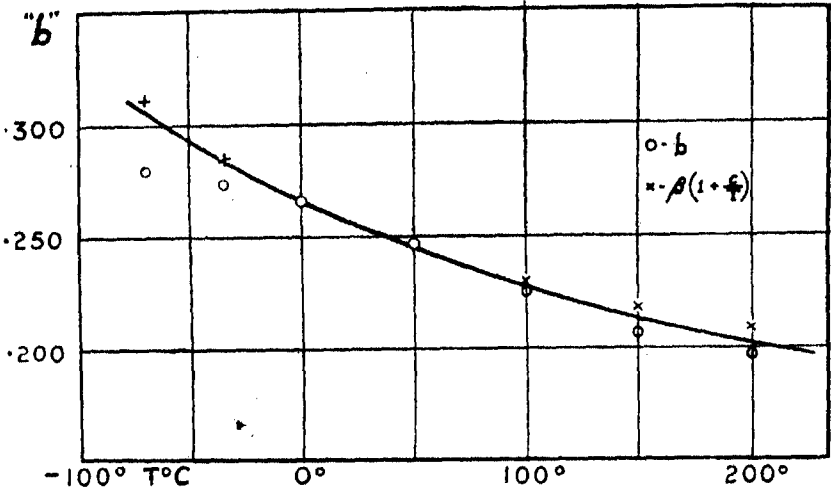


FIG. 3.

Table II.

Temperature.	"b."	$\beta (1 + 277/T).$
° C.		
- 70	0.280	0.312
- 35	0.274	0.285
0	(0.268)	0.268
50	0.246	0.245
100	0.225	0.230
150	0.207	0.218
200	0.197	0.209

to be expected, since it has been pointed out\* that Sutherland's relationship between temperature and viscosity fails completely at very low temperatures.

Table III.

Temperature.	V (obs.).	V (eq. [3A]).	V (eq. [2A]).	V (gas eq.).
° C.				
- 70	16.358	16.392	16.390	16.672
- 35	19.316	19.328	19.326	19.546
0	22.245	(22.245)	(22.245)	22.417
50	26.400	26.400	26.397	26.524
100	30.533	30.538	30.537	30.628
150	34.657	34.668	34.666	34.732
200	38.781	38.793	38.792	38.836

\* Jeans : 'Dynamical Theory of Gases,' p. 86 (1921).



In Table III, column 2 gives the experimental value of  $V$  (deduced from the data of fig. 2); column 3, the value calculated from equation (3A); column 4, that calculated from equation (2A); while the last column gives for comparison the value of  $V$  found from the simple gas equation  $pv = RT$ . It will be observed that columns 3 and 4 are practically identical. The agreement between columns 2 and 3 is within experimental error except at the lowest temperature. Since the numerical value of two of the three constants used in the calculation were obtained from viscosity data, this agreement would seem to support the assumptions made in the derivation of the equation.

Further evidence is, of course, desirable, but there are few substances for which reliable measurements of both density and viscosity are available. Accurate determinations of the density at low pressures of various organic gases have been carried out in this laboratory,\* and it is hoped presently to obtain the necessary viscosity data in order to apply them to test the equation more thoroughly.

## PART II.—THE DENSITY OF WATER VAPOUR.

### (a) *Experimental.*

*Apparatus and Procedure.*—The method employed was the same in principle as that already described, but the procedure was reversed. That is to say, the substance was first weighed, then introduced into the calibrated volume and a number of pressure readings made at various temperatures. The manometer could not be connected directly to the volume, since it was desired to heat the bath to  $200^{\circ}\text{C}.$ , and at that temperature mercury has a vapour pressure of 17 mm.† This would introduce a third component into the system; besides, it would be difficult to ensure that the equilibrium pressure of mercury vapour had been reached. Consequently, the pressure was exerted against a column of mercury in a U-tube, which was contained in a second, smaller bath, kept at a temperature just above the boiling point of the water. This pressure was balanced by admitting air to the other side of the U-tube, and the air pressure was read on the manometer. The effectiveness of this arrangement in doing away with errors due to the vapour pressure of mercury is discussed later.

The apparatus is shown diagrammatically in fig. 4, which is not drawn to scale. The main portion was constructed of Pyrex glass.  $R$  is a special Pyrex-to-soft-glass seal, which made possible an all-glass connection to the manometer,  $M$ , and the tubes,  $G_1$  and  $G_2$ , which were made of soft glass. The other con-

\* O. Maass and E. H. Boomer, *unpublished*.

† Landolt-Börnstein-Roth: 'Tabellen.'

nections between Pyrex and soft glass were through sealing-wax joints,  $I_1$ ,  $I_2$  and  $I_3$ , the construction of which is evident from the diagram.  $V$  is a Pyrex flask, the volume of which, including the tube,  $K$ , and along with that of the connecting tube,  $C$ , as far as the point marked  $X$ , was accurately determined by weighing it filled with distilled water. This was carried out with calibrated weights on a balance sensitive to 0.001 gm. The volume, at 20° C., of the connecting tube was found to be 4.3 c.c., and of the flask 1039.0 c.c. A volume-

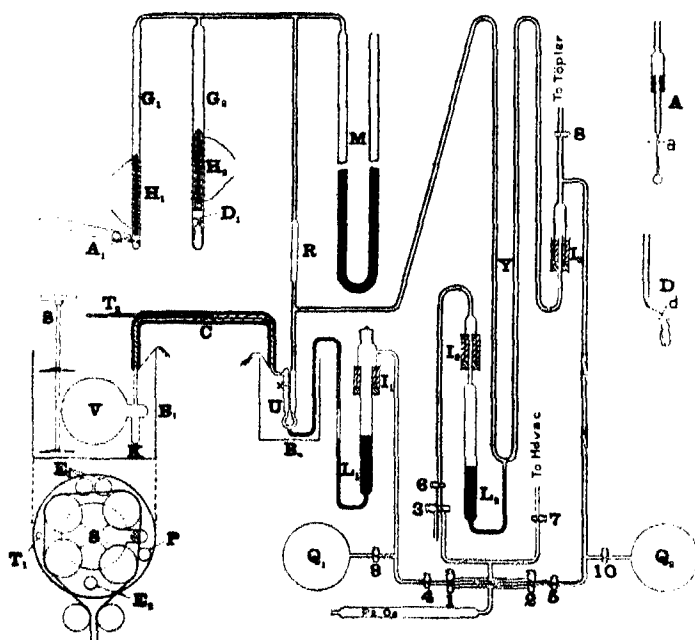


FIG. 4.

temperature curve, from which the volume of the flask at any temperature could be read, was prepared, using the formula :\*

$$V_t = V_0 (1 + 9.68 \times 10^{-6}t + 3.11 \times 10^{-9}t^2).$$

A bath,  $B_1$ , which was of metal, jacketed with a double layer of thick felt, could be placed in the position shown. The bath liquid was a high-boiling hydrocarbon oil, commercially known as "Glycoline." It fumed only slightly below 150° C., and even at 200° C. decomposition was not great, although with repeated heating it gradually became darker and somewhat more viscous. It was heated by two electrical heating elements,  $E_1$ , which were hand-regulated by means of rheostats, and a third small auxiliary heater,  $E_2$ , consisting of

\* Keyes: 'Jour. of Maths. and Phys. Mass. Inst. Tech.,' vol. 1, p. 216 (1922).

"nichrome" wire wound on a Pyrex tube and controlled by a switch, conveniently placed. Stirring was accomplished by four motor-driven brass stirrers, S. Each one carried a pair of two-bladed propellers, which were set so that two adjacent stirrers pushed up and the other two down, maintaining a constant circulation of the oil. The arrangement of heaters, stirrers, etc., in the bath is shown in plan. They were supported from above, so that the bath could be lowered and removed when necessary.

Temperatures were read by means of three mercury thermometers,  $T_1$ , calibrated by the "Physikalische-Technische Reichsanstalt" and covering the ranges  $0^\circ$ – $100^\circ$ ,  $100^\circ$ – $150^\circ$ ,  $150^\circ$ – $200^\circ$ . These were graduated in tenths and could be read to  $0.05^\circ$  very easily. The ice points of all three were tested and they were compared with each other at the points where their scales overlapped. They were found to be exact when the corrections indicated on the calibration certificates had been made.

A Heraeus, platinum in quartz, resistance thermometer, P, served to indicate variations in the bath temperature. The Wheatstone bridge already described was used in connection with this, but the Maass and Wright variable resistance was replaced by one of new design, a description of which is to be published elsewhere. It had been intended to calibrate this thermometer against the standard mercury thermometers and use it for temperature measurements, but it was not found to be sufficiently accurate; its resistance displayed a sort of "hysteresis" effect; the zero point changed irregularly after it had been heated, and its resistance at any temperature depended on the length of time taken to reach that point and on whether it had previously been heated to a higher temperature. However, when the temperature of the bath had been brought to the desired point, as read on the mercury thermometer, and the resistance adjusted until the Wheatstone bridge was balanced, the thermometer served admirably to indicate the changes of temperature in the bath. The bath was first brought to the desired temperature and the rheostats on the main heating elements adjusted so that the bath slowly cooled down with the auxiliary heater off. An attempt was made to use an adjustable thermostat of the ordinary type to control the auxiliary heater, but it was found that the lag in the action of the regulator permitted a variation in the bath temperature of as much as  $0.3^\circ$ . The method of regulating by hand was then adopted. About 1 cm. on the galvanometer scale corresponded to  $0.1^\circ$ . By the exercise of a little care it was found possible to keep the spot of light within three or four millimetres on the scale for as long a period as desired. This corresponded to a maximum variation of less than  $0.05^\circ$ .

The connecting tube, C, was covered with asbestos and wound with "nichrome" wire, through which a current was passed sufficient to heat the tube to 110–120° C. This temperature remained quite constant over the length of time necessary to take a pressure reading, and was read to the nearest degree on the thermometer,  $T_2$ .

The bath,  $B_2$ , was also heated electrically by means of a heating element similar to those used in  $B_1$  (not shown in the diagram). It was stirred by a single motor-driven glass stirrer (also not shown in the diagram), and the temperature was regulated by hand to remain approximately the same as that of the tube, C. This temperature was also read to the nearest degree on an ordinary mercury thermometer. The bath liquid was the same as used in the large bath. The Glycoline is originally quite clear and colourless and only became faintly yellow after prolonged heating at 100–120° C. The bath vessel was a four-litre Pyrex beaker. A lantern was arranged behind it, with a lens in front, which threw an image of the U-tube, U, on a ground glass screen about 4 feet away. The movement of mercury in the U-tube could thus be readily observed, and the taps controlling it were placed conveniently in front of the screen. The latter was ruled with lines 0.1 inch apart, this distance being found to correspond approximately to 0.1 cm. in the U-tube. The screen was carefully levelled before each run, with the aid of a cathetometer, so that the rulings were perfectly horizontal.

Pressure readings were made on the manometer, M, which was the same one already described (details are not shown in the figure, which is purely diagrammatic). In this case, however, the glass point was neglected and the mercury level on both sides of the manometer was read.

The remainder of the apparatus can be most clearly described in connection with an account of the experimental procedure.

A bulb of the shape shown in fig. 4 A, and of about 1–2 c.c. capacity, was filled with distilled water to the point,  $a$ , and weighed to determine its volume. It was then carefully cleaned, dried in the oven and weighed empty. A suitable amount of distilled water was introduced by means of a capillary pipette. The stem of the bulb was then forced through a one-hole rubber stopper as shown. This latter fitted closely into the end of a tube leading to a "Hyvac" motor-driven oil vacuum pump. The water was frozen with the aid of an ether-carbon dioxide mixture, and the bulb evacuated down to a pressure of 1 mm. or less. While still under vacuum it was sealed off at the point,  $a$ . The stem was removed from the rubber stopper and carefully wiped clean; when the bulb had reached room temperature it was also wiped clean and weighed

along with the stem. The bulb now contained a known weight of water, free from all but a negligible trace of air.

The end of the side tube attached to  $G_1$  being open, the bulb was introduced into the position shown in the diagram at  $A_1$ , the hammer,  $H_1$ , which consisted of an iron nail sealed into a glass tube, being raised meanwhile by means of the solenoid which is shown surrounding the tube. The open end of the side tube was then sealed off.

The tube  $G_2$  may be disregarded for the present. It was added later for a purpose which will be explained in Part III.

Taps 1, 2 and 3 being turned, as shown in the diagram, and taps 4, 5 and 6 being open, the entire apparatus could be evacuated. The preliminary evacuation was done rapidly by means of the "Hyvac" through tap 7, and evacuation was then completed by means of the automatic Töpler through tap 8. All taps were then closed; tap 3 was opened to the air, and tap 6 slowly opened, allowing the mercury in the reservoir tube,  $L_2$ , to rise into the U-tube, Y. This cuts off the main portion of the apparatus from all taps, ensuring that the vapour comes in contact only with glass and mercury, and that no air can leak in.

The bath,  $B_1$ , having previously been removed, the projecting tube, K, was immersed in liquid air, or in a carbon dioxide-ether mixture. The hammer,  $H_1$ , was raised by means of the solenoid and dropped, breaking the stem of the small glass bulb,  $A_1$ . The water distilled over through the connecting tubing and condensed in K. The pressure registered in Y and M rose to 1 cm. or so, and then slowly fell. The tube,  $G_1$ , was finally cautiously warmed with a flame to make sure that the last traces of water were gone.

The volume of all the connecting tubing had been determined in order to correct, if necessary, for any uncondensed vapour. It was approximately 125 c.c. A residual pressure of 0.1 mm. could be detected with certainty, while a pressure of 1 mm. would have meant a correction of only 0.0001 gm. Actually no residual pressure at all was registered on the manometer, and no such correction was necessary.

The water having been thus all transferred to the tube, K, air was admitted to the reservoir,  $L_1$ , by opening tap 1 to the air and cautiously opening tap 4. The mercury was thus forced through the capillary connecting tube into U. The water in V was now isolated from the rest of the system. The mercury was then drawn out of Y by opening taps 3, 6 and 7 to the "Hyvac" pump. The freezing agent could then be removed from K. The bath,  $B_1$ , was replaced and the heating elements in  $B_1$ ,  $B_2$  and on C turned on. As the pressure in

V rose, air was admitted through taps 2 and 5 to balance it on the other side of U. Air was also admitted to  $L_1$  as required to maintain the level of the mercury in U. When atmospheric pressure was reached in  $L_1$  the ground glass stopper could be removed and mercury added if required.

When  $B_2$  and C had reached a temperature of about  $110^\circ \text{C}$ .,  $B_1$  was brought to the first temperature desired. The first reading was usually made at  $125^\circ \text{C}$ ., in order to make sure that the water was completely vaporised; such higher readings as were required were then taken, after which the bath was cooled down, readings being made just above and just below  $100^\circ \text{C}$ .

The bath,  $B_1$ , being maintained at the desired temperature, as already described, tap 7 was opened to the "Hyvac," the lantern was switched on, and taps 1, 2, 4 and 5 manipulated to bring the mercury in U up to the point X, and exactly level in the two arms.  $Q_1$  and  $Q_2$  are two large volumes of about one litre each, enclosed in a box and packed in wool to maintain their temperature constant. They could be cut off from the system when desired by the taps 9 and 10, but these latter were normally open. Their volume being large compared with that of the systems to which they were connected, they served as stabilisers, facilitating control of the mercury and preventing changes in pressure due to variations in room temperature.

It was found that a difference of 0.1 mm. in the mercury levels could readily be detected on the screen and allowed for in making the pressure reading on the manometer. The latter could be read to 0.1 mm. on each side, so that the pressure readings should be accurate within 0.2 mm. The accuracy of both temperature and pressure readings is attested by the fact that on several occasions readings were repeated at the first temperature point ( $125^\circ \text{C}$ .) as the bath cooled down after being heated to  $180^\circ$  or  $200^\circ$ , and the original pressure reading was duplicated.

The possibility of mercury vapour affecting the measurements had to be taken into account, since, even at the temperature of the bath,  $B_2$ , mercury possesses an appreciable vapour pressure (about 0.7 mm.). However, the equilibrium pressure would be attained exceedingly slowly on account of the very slow diffusion of the heavy mercury atoms through the narrow tube, C, filled with gas at at least half an atmosphere pressure. The fact that two to three hours intervened between the duplicate readings just mentioned seems convincing evidence that not enough mercury vapour could have entered the volume V in the time of an experiment to affect the pressure readings materially.

The accuracy of the method is then conditioned by the accuracy with which the weight of the water was known. The amounts of water used varied from

0.25 to 0.60 gm., and weighings were made to 0.0001 gm. In the handling which the stem of the bulb necessarily received in inserting it in the rubber cork and removing it again it was difficult to make certain that no grease or tiny fragments of rubber adhered to the glass. However, this method of preparing the water samples commended itself on account of its simplicity, and great care was taken to clean bulb and stem as thoroughly as possible before weighing. Even admitting a possible error of 0.0003 gm. in the weight of the water, the probable accuracy of the measurements is about 1 in 1,000 at the lowest pressures to 1 in 2,000 at the highest.

When the desired readings had been obtained the mercury was drawn back from U into L<sub>1</sub> by opening taps 4, 1 and 7. Tap 7 was then closed for a moment, while taps 2, 3, 5 and 6 were opened to the suction line. Tap 7 was re-opened and the whole system evacuated, whereupon the heaters and stirrers were switched off and the run was over.

*Results.*—The results obtained are given in detail in Table IV. The first column contains the temperature, the second the corrected mass, the third the pressure in terms of mercury at 0° C., the fourth column the volume, and the last the apparent molecular weight. As in Part I, the values of  $M_1$  are shown plotted against pressure in fig. 5.

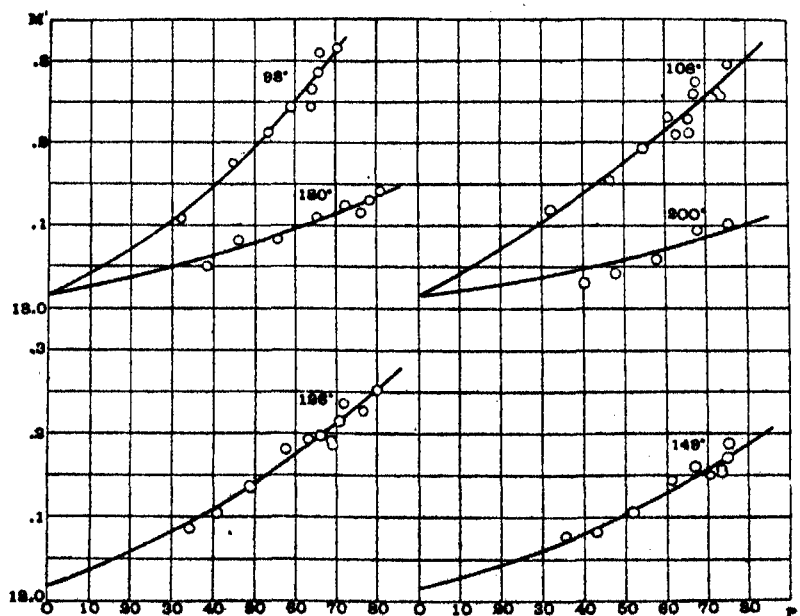


FIG. 5.

Table IV.

Temperature.	Mass.	Pressure.	Volume.	M'.
° C.	gm.	mm.	c.c.	
94.3	0.2571	312.4	1039.7	18.142
98.4	0.2571	316.4	1039.8	18.109
107.8	0.2571	324.3	1039.9	18.116
126.0	0.2570	340.1	1040.1	18.089
148.6	0.2569	359.4	1040.3	18.076
180.6	0.2569	387.1	1040.7	18.051
199.9	0.2568	403.7	1040.9	18.033
81.8	0.3059	358.4	1039.6	18.182
125.9	0.3058	404.2	1040.1	18.106
148.5	0.3058	427.5	1040.3	18.085
180.4	0.3057	459.7	1040.7	18.081
200.1	0.3056	480.3	1040.9	18.043
98.3	0.3687	452.0	1039.8	18.175
107.8	0.3686	463.9	1039.9	18.156
126.0	0.3686	486.5	1040.1	18.136
148.5	0.3685	514.6	1040.3	18.106
180.6	0.3684	554.1	1040.7	18.085
199.9	0.3683	578.1	1040.9	18.063
98.2	0.4369	534.4	1039.8	18.213
107.8	0.4369	548.7	1039.9	18.194
126.0	0.4368	575.1	1040.1	18.181
148.5	0.4367	608.5	1040.3	18.146
180.6	0.4366	655.7	1040.7	18.108
199.9	0.4365	683.9	1040.9	18.095
98.2	0.4828	589.6	1039.8	18.243
107.7	0.4827	605.0	1039.9	18.229
126.0	0.4826	635.0	1040.1	18.193
148.5	0.4825	671.8	1040.3	18.159
180.6	0.4823	723.9	1040.7	18.121
200.0	0.4822	755.5	1040.9	18.098
94.2	0.5060	609.4	1039.7	18.301
107.8	0.5059	634.7	1039.9	18.212
125.9	0.5058	665.3	1040.1	18.197
148.6	0.5057	704.5	1040.3	18.152
180.6	0.5055	758.8	1040.7	18.118
98.2	0.5236	638.6	1039.8	18.266
107.8	0.5235	656.1	1039.9	18.231
126.0	0.5234	688.6	1040.1	18.191
148.5	0.5233	728.6	1040.3	18.159
180.6	0.5233	784.8	1040.7	18.131
98.3	0.5243	640.3	1039.8	18.245
107.8	0.5243	657.7	1039.9	18.213
126.0	0.5241	689.8	1040.1	18.187
148.6	0.5240	729.8	1040.3	18.155
98.3	0.5374	655.0	1039.8	18.284
107.8	0.5374	672.6	1039.9	18.258
125.9	0.5373	706.0	1040.1	18.215
148.6	0.5371	747.5	1040.3	18.171
180.6	0.5370	805.2	1040.7	18.137



Table IV—*contd.*

Temperature.	Mass.	Pressure.	Volume.	M'.
° C.	gm.	mm.	c.c.	
98·3	0·5428	660·7	1039·8	18·308
107·8	0·5428	678·7	1039·9	18·274
126·0	0·5427	712·4	1040·1	18·236
148·6	0·5425	754·2	1040·3	18·189
98·3	0·5792	704·2	1039·8	18·315
107·8	0·5791	724·5	1039·9	18·263
125·8	0·5790	760·2	1040·1	18·220
107·8	0·5846	731·7	1039·9	18·258
107·8	0·6079	759·1	1039·0	18·298
126·0	0·6078	797·1	1040·1	18·253

In making the calculation of M' allowance has to be made for the small portion of the total volume which is at a different temperature from that of the main bath. This is done by calculating the mass of water vapour which will be contained in the connecting tube, C, and in the upper part of U, at the pressure observed, and subtracting it from the total mass. This is made clear in the specimen calculation which follows:—

Temperature of bath, B <sub>1</sub> .. ..	180·6° C.	453·7° K.
Temperature of tube, C .. ..	135° C.	
Temperature of bath, B <sub>2</sub> .. ..	118° C.	
Mean temperature of C and B <sub>2</sub> .. ..	126° C.	399° K.
Temperature of room .. ..	26° C.	
Pressure observed .. ..	788·5 mm.	
Correction for room temperature .. ..	3·7	
Corrected pressure .. ..	784·8 mm.	
Volume of C and U to point X .. ..	4·3 c.c.	
Mass of water vapour in C and U, $m = \frac{Mpv}{RT}$		
$m = \frac{18 \times (785/760) \times 0·0043}{0·082 \times 399}$		= 0·0024 gm.
Weight of bulb filled with water .. ..	4·98 gm.	
Weight of bulb empty .. ..	4·25	
Volume of bulb .. ..	0·73 c.c.	

Weight of bulb and water sample ..	4.7752 gm.
Weight of bulb empty .. .. .	4.2505
	<hr/>
	0.5247
Correction for air in empty bulb ..	0.0009
	<hr/>
Weight of water sample .. .. .	0.5256 gm.
Weight of water vapour in C and U ..	0.0024
	<hr/>
Net weight of water vapour in V ..	0.5232 gm.
Volume of V at 180° C. .. .. .	1040.7 c.c.

$$M' = m \frac{RT}{pv} = \frac{0.5232 \times 0.08209 \times 453.7}{(784.8/760) \times 1.0407} = 18.131.$$

(b) *Theoretical.*

*The Existence of Association in Water Vapour.*—The problem of the molecular constitution of liquid water has been attacked from many points of view, and the generally accepted conclusion is that at temperatures near the freezing point it consists largely of "trihydrol," with an admixture of "dihydrol," while at temperatures near the boiling point the equilibrium is represented by  $(H_2O)_2 \rightleftharpoons 2H_2O$ , the dihydrol being in excess.\*

If this is the case, it would be anticipated that water vapour, in the vicinity of the boiling point at least, should contain an appreciable proportion of dihydrol molecules. Very little direct evidence on this point is available. Bose† has published some calculations, based on experimental work of Kornatz,‡ which led him to the conclusion that water is associated to the extent of about 9 per cent. for the saturated vapour at 100° C. Oddo§ has also published calculations based on density values deduced by means of the Clausius-Clapeyron equation from the experimental work of Regnault. He arrived at the astonishing conclusion that, while water vapour is associated above 32° C., below that temperature it is dissociated into its ions. It is scarcely necessary to discuss the work of these authors, since the subject has recently been very thoroughly reviewed by Kendall|| and Menzies.|| Kendall points out that the fundamental fallacy in such calculations is the neglect of the equation of state correction.

\* Symposium on Water: 'Trans. Faraday Soc.,' vol. 6 (1910).

† 'Zeit. Elektrochem.,' vol. 14, p. 269 (1908).

‡ Inaug. Diss., Königsberg (1908).

§ 'Gazz. Chim. Ital.,' i, 45, 319 (1915).

|| Loc. cit.

He also indicates the existence of a systematic discrepancy between Bose's equation for the equilibrium,  $2\text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{O})_2$ , and the experimental results which are quoted in support of it. He concludes that the evidence for the existence of such an equilibrium in the vapour phase is insufficient. Menzies draws attention to the uncertainty involved in the practice, employed by Bose, of stating vapour densities in terms of the density of air. He demonstrates Oddo's conclusions to be illusory by repeating the latter's calculations, using more modern experimental data in the Clausius-Clapeyron equation. He also deduces from the vapour pressure measurements of Perman\* and Krauskopf† a value for the density of the saturated vapour at 73° C., only 0.1 per cent. above the ideal value. The Clausius-Clapeyron equation, at the same temperature, gives a figure of 0.9 per cent. higher than the ideal. While admitting the discrepancy, Menzies suggests that if the error be distributed equally between the two methods, the mean, 0.45 per cent., is almost exactly the deviation from the ideal gas density required at this temperature by Berthelot's modification of van der Waals' equation, and that "the numerical basis remaining from which to postulate polymerisation of water vapour at this temperature is precisely zero."

However, the methods employed by Menzies in arriving at this result are, in his own words, "at best, rather indirect." Direct evidence is afforded by the data of Table V.

Table V.

Temp.	V (obs.).	V (Ber.).	V (eq. [3A]).	M' (obs.).	M' (calc.).
° C.	Pressure = 1 atmosphere.				
97.9	29.920*	30.159	30.208	18.338*	18.163
107.9	30.817	30.996	31.038	18.284	18.154
125.9	32.355	32.509	32.530	18.238	18.140
149.9	34.338	34.417	34.436	18.175	18.123
179.9	37.043	37.078	37.084	18.126	18.105
199.9	38.654	38.653	(38.654)	18.097	(18.097)

\* Extrapolated.

Column 5 contains the apparent molecular weights for 1 atmosphere pressure, read from the isothermal curves of fig. 5. Column 2 gives the corresponding volumes for 1 gram molecule, obtained by means of the relation,

$$V = \frac{18.016}{M'} \cdot \frac{RT}{p}. \quad \text{In column 3 are the values of } V \text{ calculated by means of the}$$

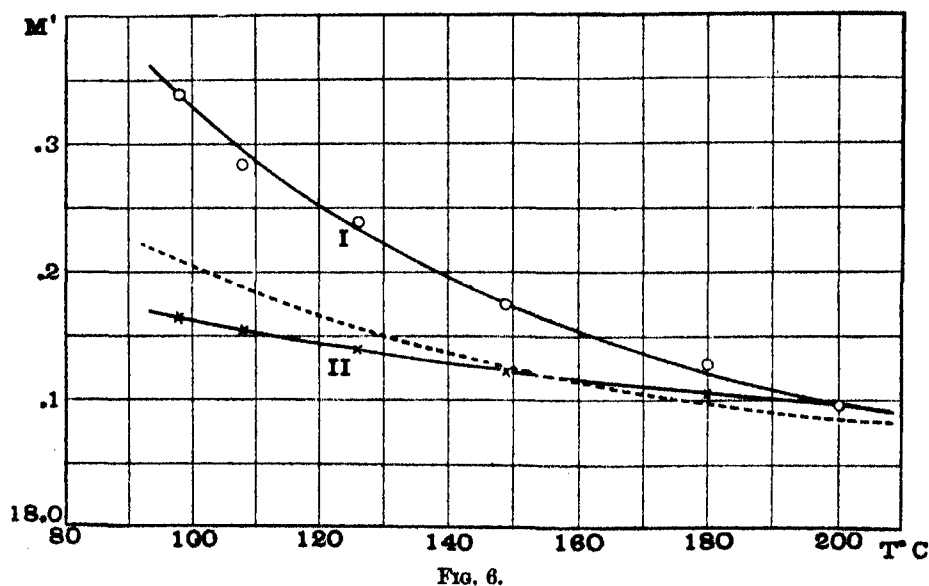
\* 'Roy. Soc. Proc.,' vol. 72, p. 72 (1903).

† 'J. Phys. Chem.,' vol. 14, p. 489 (1910).

Berthelot equation, using the critical constants of Holborn and Baumann\* employed by Menzies. It will be seen that, while the calculated value agrees perfectly with experiment at 200°, at the lower temperatures there is a discrepancy considerably greater than the experimental error of the observations.

Column 4 gives the values of  $V$  obtained from equation (3A). The value of  $r$ , the radius of the water molecule, stated by Jeans,† is  $2.29 \times 10^{-8}$  cm. Very few experimental data are available on the viscosity of water vapour. Vogel‡ gives for Sutherland's constant, " $c$ ," a value 548, which he deduces by means of an empirical relationship connecting  $c$  with critical temperature. This gives  $\beta = 0.086$ . Assuming that, if polymerisation exists, dissociation is complete at the highest temperature, 200° C., and inserting the experimental data for that temperature in the equation, " $a$ " is found to be 13.95. These constants are then employed to calculate  $V$  for the remaining temperatures. The apparent molecular weights,  $M'$ , corresponding to these values of  $V$ , are given in the last column of the table.

It is clear that this equation also fails to fit the experimental facts. The data of columns 5 and 6 are represented graphically in fig. 6, curve I being the



experimental and curve II the theoretical. The discrepancy is very marked, and the inference is that some degree of association exists.

\* 'Ann. Physik,' vol. 31, p. 945 (1910).

† *Loc. cit.*

‡ 'Ann. Physik,' vol. 43, p. 1235 (1914).

Further, it will be observed that the isotherms of fig. 5 are this time not straight lines, but curve upward away from the pressure axis. It is true that equation (5A) is only an approximation and that equation (5) would give a curve of this type. But to account for the curvature actually observed an absurdly high value of "a" would be required. That it may be accounted for by postulating the existence of associated molecules is made clear by the following considerations.

Assuming for the moment the ideal gas law to hold, the equation is obtained\*

$$\frac{M(M' - M)}{(2M - M')^2} = Kp, \quad (6)$$

where  $M'$  is the observed "apparent" molecular weight,  $M$  is the theoretical molecular weight, and  $K$  is a constant. The fraction associated is given by

$$\alpha = \frac{M' - M}{M'}. \quad (7)$$

Combining equations (5A) and (6), there is obtained

$$\frac{M \{M' - M(1 + Ap)\}}{\{2M(1 + Ap) - M'\}^2} = K'p. \quad (6A)$$

The degree of association is

$$\alpha = \frac{M' - M(1 + Ap)}{M'}. \quad (7A)$$

The difference  $(M' - M)$  is to a first approximation proportional to  $p$ , so that the resulting isotherm is still experimentally indistinguishable from a straight line. But this is based on the assumption of an "a" and "b" which are independent of pressure. We are actually dealing with what is, in effect, a mixture of two gases, monohydrol and dihydrol. Van der Waals gave, for a mixture of two gases present in the molecular ratio,  $x/1 - x$ , the relation†

$$\begin{aligned} a &= a_1(1 - x)^2 + 2a_{12}x(1 - x) + a_2x^2. \\ b &= b_1(1 - x)^2 + 2b_{12}x(1 - x) + b_2x^2. \end{aligned}$$

Since the ratio,  $x/1 - x$ , in the present case varies with pressure (and temperature), "a" and "b" are really functions of  $p$  and  $T$ , which involve the unknown constants,  $a_{12}$ ,  $b_{12}$ ,  $a_2$  and  $b_2$ . To account for the form of curve obtained, "a" must increase with pressure and increase more rapidly than "bRT."

Since increasing pressure favours association, this would indicate that the dihydrol molecules possess a much larger external field of force and consequently larger power of attraction than the monohydrol molecules. This fact

\* Cf. Nernst, 'Theoretische Chemie,' p. 525 (1921).

† Nernst, 'Theoretische Chemie,' p. 262 (1921).

emphasises the sharp distinction to be drawn between the effect of molecular attraction and the effect of association. Molecular attraction increases the number of collisions and may even cause two molecules to travel temporarily together, but without material alteration in their structure. In the case of association or polymerisation, two or more molecules of the same substance come together, with an actual rearrangement of their electrons, to form what is really a new chemical individual with new and characteristic properties.

While the above considerations indicate the existence of polymerised molecules in water vapour, an exact quantitative measure of the degree of association is rendered quite impossible, since there is no way of determining just how "*a*" and "*b*" will vary with pressure and temperature. However, although an exact determination from the above data is not possible, an estimate of the degree of association may be obtained from equation (7A), putting in place of  $M(1 + Ap)$  the value of  $M'$  taken from the last column of Table V. This gives, at 108° C., 0·71 per cent., and at 98° C. (supersaturated vapour at 1 atmosphere pressure), 0·95 per cent.

The figures in column 6 of Table V were obtained by starting with the gratuitous assumption that no association exists at 200° C. This is probably not quite correct, and consequently the value of "*a*" derived on that assumption is too large. However, it is obvious from fig. 6 that the degree of association increases rapidly with lowering of the temperature. From the consideration discussed above it follows that the value of "*a*" should rise as the temperature falls. Curve II should probably have somewhat the form shown by the dotted curve. Consequently the figures stated above for the degree of association in the neighbourhood of 100° are a probable maximum.

It is worth noting that a similar figure is obtained from Menzies' data, if the Clausius-Clapeyron equation be accepted as the more reliable of his methods of calculating density. He states\* that it leads to a value for the saturated vapour at 73° C., 0·9 per cent. higher than the ideal density. Equation (3A) gives a value only 0·33 per cent. above the ideal. If the difference, 0·57 per cent., is attributed to association, the result is in good agreement with the above.

\* *Loc. cit.*, p. 856.

## PART III.—THE SYSTEMS WATER CARBON DIOXIDE AND WATER AMMONIA.

(a) *Experimental.*

*Apparatus and Procedure.*—The water was weighed out in a small bulb exactly as before. The amount was chosen to give a pressure of approximately half an atmosphere at the highest temperature desired. The carbon dioxide and the ammonia could not, of course, be weighed out in this simple manner, so recourse was had to the apparatus described in Part I. The procedure was identical with that already employed; only the calculation was reversed. That is, the value of  $M'$  for the pressure and temperature ( $20^{\circ}$  C.) employed was read from the graph and the mass of substance condensed in the bulb calculated from the formula

$$m = \frac{pv}{RT} M'.$$

The calibrated globe cracked at the beginning of the experiments and had to be replaced. The volume of the new one was determined by weighing it filled with distilled water, using the same balance and weights as before. A test experiment was carried out by weighing one bulb in the manner described in Part I. The result was :—

Weight of carbon dioxide calculated	..	..	1.0436 gm.
Weight of carbon dioxide found	..	..	1.0434 gm.

The agreement is well within the limit of experimental error. This offers convincing proof of the accuracy of this method of obtaining a known amount of carbon dioxide, and, incidentally, furnishes an additional point on the  $20^{\circ}$  isotherm of fig. 1.

The bulbs used were of the shape shown in fig. 4D. They were sealed off at  $d$  and allowed to warm up to room temperature and to stand for some time in case any flaw existed in the glass which might lead to an explosion. The pressure of gas introduced into the calibrated volume could be controlled very exactly, and it was easy to make a rough estimate of the amount necessary to give any desired pressure in the new density apparatus. The amount in each bulb was regulated to give approximately the same pressure as the corresponding water bulb.

The tube  $G_2$  (fig. 4) was cut off near the top; the bulb containing carbon dioxide or ammonia was slid cautiously into it ( $D_1$ ), and the contents of the bulb frozen by dipping the end of  $G_2$  in liquid air. The hammer,  $H_2$ , was then slid in on top of the bulb and  $G_2$  sealed back in place on the apparatus.

The water bulb,  $A_1$ , being already in place and  $G_1$  sealed off,  $D_1$  was allowed to warm up, the lower end of  $G_2$  being surrounded by a shield in case of accident, and the whole apparatus was evacuated thoroughly.

The remainder of the procedure was the same as already described. When the water had been completely condensed in  $K$ ,  $D_1$  was again frozen by immersing the lower part of  $G_2$  in liquid air, and the stem was broken by raising and dropping the hammer,  $H_2$ , by means of the solenoid. As  $D_1$  warmed up the carbon dioxide or ammonia came over and was condensed on top of the water in  $K$ . Again no residual pressure correction was found necessary. When condensation was complete the mercury was run into  $U$ , and the remainder of the experiment proceeded exactly as when water alone was under investigation.

*The Density of Carbon Dioxide up to 200° C.*—It was, of course, possible to introduce into the apparatus in the manner described carbon dioxide or ammonia alone. The data given in Part I do not cover the entire temperature range over which the two-component system was to be investigated, so, in order to avoid the necessity of extrapolating the curve of fig. 2, one run was made on carbon dioxide alone with the new apparatus.

The results are shown in Table VI. The method of calculation is exactly similar to that illustrated in Part II.

Table VI.

Temp.	Pressure.	Weight.	Volume.	$M'$ .	$M'_{760}$ .
° C.	mm.	gm.	c.c.		
98.2	600.0	1.1878	1039.8	44.107	44.136
107.8	615.0	1.1876	1039.9	44.123	44.152
125.9	644.5	1.1873	1040.1	44.088	44.104
148.5	680.7	1.1871	1040.3	44.093	44.104
180.6	723.3	1.1868	1040.7	44.075	44.078
199.9	763.7	1.1866	1040.9	44.050	44.050

The last column gives the value of  $M'$  at 1 atmosphere pressure, obtained from those in the previous column by applying equation (5A). These are the points marked with crosses in fig. 2. Except for the one point (108°) they fall closely on the smooth curve, which is a continuation of that already obtained for the lower temperatures. The point at 98° confirms exactly the previous determination with the old apparatus.

*The Density of Ammonia.*—The ammonia was obtained by warming the concentrated aqueous solution and condensing the product with ether-carbon dioxide, after passing it through a drying tower containing solid potassium



hydroxide. It was then distilled a number of times over dry potassium hydroxide, and finally absorbed in ammonium thiocyanate,\* from which it could be regenerated as required by gently warming the bulb which contained it.

As a preliminary step it was necessary to determine the molecular weight-pressure isotherm at a convenient temperature by means of the apparatus and procedure described in Part I. These results are stated in Table VII, where the various columns have the same significance as in Table I.

Table VII.

Temperature.	Pressure.	Weight.	Volume.	M'.
° C.	mm.	gm.	c.c.	
19.1	734.7	0.7753	1116.7	17.227
19.7	738.5	0.7771		17.213
	736.0	0.7757		17.240
	692.4	0.7289		17.220
	576.0	0.6047		17.173
	523.6	0.5502		17.180
	482.4	0.5059		17.155
	388.8	0.4078		17.157

The figures in the last column are shown plotted against pressure in fig. 7. The values of M' used in calculating the weight of ammonia in the bulbs prepared for introduction into the new apparatus were read from the graph.

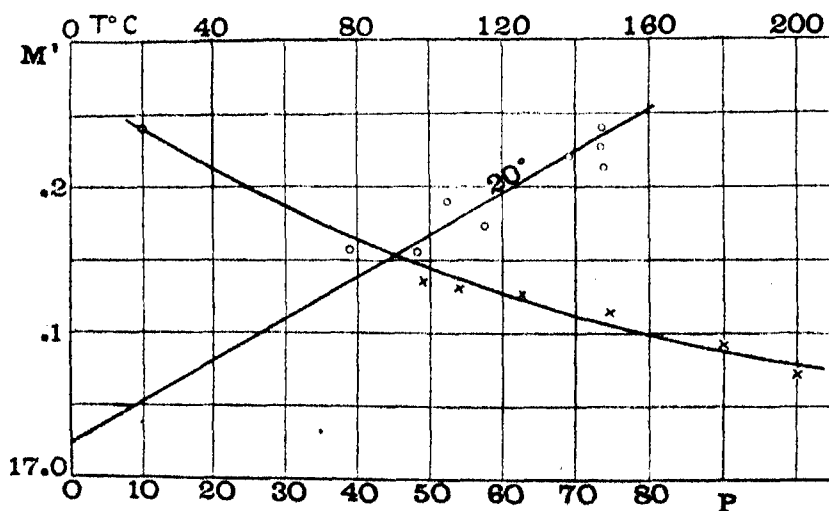


FIG. 7.

\* Foote and Brinkley, 'Jour. Am. Chem. Soc.,' vol. 43, p. 1179 (1921).

A determination of the density of ammonia over the range 98°–200° C. was made with the new apparatus. The results are stated in Table VIII, in which the columns have the same significance as in Table VI. The figures in the last column are shown plotted against temperature in fig. 7. Values for lower pressures at any desired temperature were derived from the figure for that temperature read from the curve by applying equation (5A).

Table VIII.

Temp.	Pressure.	Weight.	Volume.	M'.	M' <sub>760</sub> .
° C.	mm.	gm.	c.c.		
98.1	028.4	0.4828	1039.8	17.112	17.136
107.8	644.6	0.4827	1039.9	17.111	17.131
125.9	675.0	0.4826	1040.1	17.113	17.127
148.5	713.2	0.4826	1040.3	17.107	17.114
180.5	767.5	0.4824	1040.7	17.092	17.091
199.9	800.6	0.4823	1040.9	17.077	17.073

*Results for Two-Component Systems.*—The results for the water carbon dioxide system are stated in Table IX, and for water ammonia in Table X. The headings of the columns are self-explanatory. The partial pressures of the individual components are obtained simply by reversing the calculation illustrated in Part II.

Table IX.

Temp.	$P_{H_2O}$ .	$P_{CO_2}$ .	$P_{calc.}$	$P_{obs.}$	Difference.
° C.	mm.	mm.	mm.	mm.	mm.
98.2	380.9	367.1	748.0	747.1	0.9
107.8	390.7	376.4	767.1	766.0	1.1
	Weight of water = 0.3111 gm.		Weight of CO <sub>2</sub> = 0.7288 gm.		
	Weight of water = 0.2674 gm.		Weight of CO <sub>2</sub> = 0.6971 gm.		
94.2	323.9	347.3	671.2	669.6	1.6
98.2	327.0	351.1	679.0	676.8	2.2
107.8	336.2	360.1	696.3	694.2	2.1
126.0	352.2	377.2	729.4	727.6	1.8
148.5	372.4	398.3	770.7	769.1	1.6
	Weight of water = 0.2550 gm.		Weight of CO <sub>2</sub> = 0.6130 gm.		
98.2	312.6	308.8	621.4	620.0	1.4
107.8	320.6	316.7	637.3	635.9	1.4
125.9	336.0	331.6	667.6	666.4	1.2
148.5	355.2	350.3	705.5	704.0	1.5
180.5	382.4	376.8	759.2	758.0	1.2

Table X.

Temp.	$p_{H_2O}$ .	$p_{NH_3}$ .	$p_{calc.}$	$p_{obs.}$	Difference.
Weight of water = 0.2505 gm.    Weight of $NH_3$ = 0.2485 gm.					
° C.	mm.	mm.	mm.	mm.	mm.
98.2	306.9	323.1	630.0	625.8	4.2
107.8	314.8	331.5	646.3	642.0	4.3
125.9	330.0	347.3	677.3	673.6	3.7
148.5	348.9	366.8	715.7	712.1	3.6
180.5	375.4	394.1	769.5	767.0	2.5
Weight of water = 0.2900 gm.    Weight of $NH_3$ = 0.2765 gm.					
98.2	355.0	359.4	714.4	708.6	5.8
107.8	364.1	368.8	732.9	727.0	5.9
125.9	382.0	386.2	768.2	763.0	5.2
148.5	403.6	407.7	811.5	806.9	4.6

(b) *Theoretical.*

*Discussion of Results.*—The figures in the last column of Tables IX and X represent the deviations from Dalton's Law, *i.e.*, from the behaviour of an ideal gas mixture, brought about by the mutual attraction of the two molecular species present. The data from which the partial pressures are calculated are accurate to about 0.05 per cent., so that the total calculated pressure is subject to a possible error of about 0.3 mm. An accuracy of 0.2 mm. is all that is claimed for the observed pressure, so that the differences may suffer from an error of 0.4 to 0.5 mm. This being the case, no attempt is made to draw other than qualitative conclusions.

The attraction exhibited between water vapour and carbon dioxide is quite small, in contrast to the strong attraction evidenced by the ready solubility of carbon dioxide in liquid water. The pressure deviation observed is considerably smaller, for instance, than that found by Maass and Morrison\* at room temperature for methyl ether and carbon dioxide. No actual compound formation can be anticipated in the latter case, so it is concluded that no  $H_2CO_3$  molecules are formed in the vapour state. A decrease in the mutual attraction, with rising temperature, seems to be indicated, but the variation is too small to be distinguished with any certainty from experimental error.

The attraction between water vapour and ammonia is considerably larger, as would be anticipated from the greater solubility of ammonia in liquid water. It is still, however, surprisingly small, being of just the same order as that between methyl ether and carbon dioxide (4.3 mm.) already mentioned. No

\* *Loc. cit.*

appreciable number of  $\text{NH}_4\text{OH}$  molecules can be formed. In this case the decrease in attraction with rising temperature is unmistakable and is quite large in proportion to the total effect.

All these facts are readily explicable on the basis of the conclusions arrived at in Part II, namely, that water vapour at the boiling point contains a small proportion of dihydrol molecules, that the proportion diminishes rapidly as the temperature rises (the pressure being constant), and that the highly polar character attributed to water is a property of the dihydrol molecule, while monohydrol is relatively non-polar. Hence the comparatively small attraction for carbon dioxide and ammonia displayed in the vapour state and the rapid diminution of the existing attraction as the temperature rises.

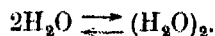
It is hoped to extend measurements of this character to include various series of gaseous mixtures and thereby to secure data which may be made to throw light on questions of molecular structure.

#### SUMMARY.

1. The density of carbon dioxide has been measured with an accuracy of 0.05 per cent., at pressures up to 1 atmosphere and over the range,  $-70^\circ\text{C}$ . to  $200^\circ\text{C}$ .

2. The equation of van der Waals has been deduced from a somewhat new point of view, and the deduction is also shown to lead to a quadratic equation, which is valid over the range for which the mean free path equation holds. The " $b$ " of van der Waals is shown to be a function of temperature and is related to the mean free path. The " $b$ " determined from the experimental results for carbon dioxide is found to vary with temperature in the manner indicated. Using constants derived from viscosity data, the equation is proved to reproduce satisfactorily the experimental results quoted.

3. The density of water vapour has been measured with an accuracy of at least 0.1 per cent., at pressures up to 1 atmosphere and over the temperature range,  $98^\circ\text{C}$ . to  $200^\circ\text{C}$ . The results show greater divergence from the ideal density than can be accounted for on the basis of the equation of state and the hypothesis of polymerisation is adopted, the molecular condition of water vapour being assumed to be represented by the equilibrium,



A sharp distinction is drawn between association and the equation of state effect, but it is demonstrated that an exact calculation from the results quoted, of their separate influence in producing the deviation from ideal density, is not

possible. An approximate estimate of the degree of association in the vicinity of 100° C. and 1 atmosphere pressure is given. It is of the order of 0.9 per cent. and probably rather less.

4. It is concluded that the highly polar character attributed to water is a property of the dihydrol molecule, while monohydrol is relatively non-polar.

5. Measurements have been carried out of the deviations from Dalton's Law at a pressure of about 1 atmosphere and temperatures between 98° C. and 200° C. in approximately equimolecular mixtures of water vapour and carbon dioxide and water vapour and ammonia. The mutual attraction of the components in these systems is relatively small. The results are in complete accord with the foregoing conclusions regarding the molecular constitution of water vapour.

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*Wave Resistance: Some Cases of Unsymmetrical Forms.*

By T. H. HAVELOCK, F.R.S.

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1. One of the chief features of interest in curves showing the variation of wave resistance with velocity is the occurrence of oscillations about a mean curve, which may be regarded as due to interference between the waves produced by the front and rear portions of the model. In various comparisons made between theoretical curves and such suitable experimental results as are available, the greatest divergence is perhaps in the magnitude of these oscillations, the theoretical curves showing effects many times greater than similar experimental results. There are, no doubt, many approximations in the hydro-dynamical theory which preclude too close a comparison between theoretical and experimental results in any particular case, but it seems fairly certain that the divergence in question must be largely due to neglecting the effects of fluid friction. For several reasons it is useless to attempt at present a direct introduction of viscosity into the mathematical problem, but a consideration of its general effect suggests one or two calculations which may be of interest. The direct effect of viscosity upon waves already formed may be assumed to be relatively small; the important influence is one which makes the rear portion of the model less effective in generating waves than the front portion. We may imagine this as due to the skin friction decreasing the general relative velocity of model and surrounding water as we pass from the fore end to the aft end; or we may picture the so-called friction belt surrounding the model, and may consider the general effect as equivalent to a smoothing out of the curve of the rear portion of the model. Without pursuing these speculations further, they suggest calculations which can be made for models in frictionless liquid when the form of the model is unsymmetrical in this manner; and the particular point to be examined is the effect of such modification upon the magnitude of the interference phenomena.

The first sections compare, in this respect, two bodies entirely submerged in the liquid. The form in each case is a surface of revolution; one is symmetrical fore and aft and has sharp pointed ends, while in the other the rear portion is cut away so as to come to a fine point. By inspection of the expressions for the wave resistance it is seen that the oscillating terms are of a lower order of magnitude in the latter than in the former case.

The remaining sections deal with the similar problem for a model of infinite draught and constant horizontal cross-section; the forms of the section for the two cases are shown in fig. 1. Here, with the help of tables and graphs available from previous studies, the expressions for the wave resistance have been graphed and the curves are shown in fig. 2. The result of smoothing the lines of the rear portion is very marked. It makes the curve like experimental ones in this respect at least, that the curve is a continually ascending one in the range shown; the superposed oscillations are not large enough to make actual maxima and minima. A more complete study of the progressive effect of small changes in the rear half of the model would involve very lengthy calculations; the examples given have been chosen for the comparatively simple form of the mathematical expressions. It is to be understood that they are not intended as a direct representation of the actual effects of fluid friction; but they show the great difference in interference effects which are produced by an asymmetry of the general nature suggested by them.

2. The fluid motion produced by a body entirely submerged in a uniform stream may be investigated by the method of successive images. The first approximation consists of the distribution of sources and sinks which is the image of the uniform stream in the surface of the body; the second is the image of these sources and sinks in the upper free surface of the stream, and the process could be carried on by successive images in the surface of the body and the free surface of the stream. After the second stage the expressions become very complicated, as the image of a single source in the upper free surface is a distribution of infinite extent along a horizontal line at a height above the free surface equal to the depth of the source. It would be of interest to carry the process further in some simple cases, but at present the second stage must suffice; it can be seen that, in general, this implies that the ratio of the maximum vertical diameter of the body to its depth below the surface must be small.

For the first stage of the approximation, instead of finding the image system for a given form in a uniform stream, it is more convenient to begin with a given distribution of sources and sinks and deduce the form of the body. As we shall deal only with surfaces of revolution, we assume a line distribution of finite extent along a line parallel to the stream. Writing down Stokes' current function, the form of the body may be found by graphical methods devised by Rankine and applied to shiplike forms by D. W. Taylor and other writers.

Let the stream, of velocity  $c$ , be parallel to  $Ox$ , and let there be a source

distribution of strength  $f(x)$  along portion of the axis of  $x$ ; then, with  $\tilde{\omega}$  as distance from  $Ox$ , the velocity potential and stream function are given by

$$\phi = cx + \int \frac{f(h) dh}{\{(x-h)^2 + \tilde{\omega}^2\}^{\frac{1}{2}}} \quad (1)$$

$$\psi = \frac{1}{2}c\tilde{\omega}^2 + \int \frac{(x-h)f(h) dh}{\{(x-h)^2 + \tilde{\omega}^2\}^{\frac{3}{2}}} \quad (2)$$

The form of the solid is obtained from the equation  $\psi = 0$ . The graphical method is first to graph the integral in (2) upon  $\tilde{\omega}$  as a base for given values of  $x$ , obtaining a family of curves each corresponding to a constant value of  $x$ ; then on the same diagram the parabola  $\psi = \frac{1}{2}c\tilde{\omega}^2$  is drawn. The intersections of the parabola with the family of curves give pairs of corresponding values of  $x$  and  $\tilde{\omega}$  on the zero stream line.

It is obvious that if  $f(h)$  is finite, not zero, at an end of the range of sources then the body has a blunt end; and further, the length of the body is greater than the length of the range. If  $f(h)$  is zero at both ends, the body has a sharp point at both ends and its length is equal to the length of the range; if, in addition,  $f'(h)$  is zero at an end, the sharp point at that end is one of zero angle.

3. In considering the second approximation, namely, the image of the distribution  $f(h)$  in the upper free surface of the stream, it is more convenient to use as the elementary system a doublet with its axis parallel to the stream. As we are dealing with solid bodies of finite size, we can in general replace the line of sources and sinks by an equivalent line of doublets; thus instead of (1) we have

$$\phi = cx + \int \frac{(x-h)\psi(h)dh}{\{(x-h)^2 + \tilde{\omega}^2\}^{\frac{3}{2}}}, \quad (3)$$

provided  $\psi'(h) = f(h)$ , and  $\psi(h)$  is zero at both limits. Consider now a solid of revolution with its axis horizontal and at a depth  $f$  below the surface, the form being such that the image of the uniform stream in it is a line of doublets of moment  $\psi(h)$ . The image of this system in the free surface can be shown to be a certain distribution of doublets of infinite extent along a line at a height  $f$  above the surface. For the present purpose we shall quote the expression for the wave resistance\*

$$R = 16\pi g^4 \rho c^{-8} \int \psi(h) dh \int \psi(h') dh' \int_0^{\pi/2} \sec^5 \phi \times \cos \left[ \{g(h-h')/c^2\} \sec \phi \right] e^{-(2gf/c^2) \sec^2 \phi} d\phi. \quad (4)$$

\* 'Roy. Soc. Proc.,' A, vol. 95, p. 363 (1919).



We shall consider two cases, one a sharp-ended form which is symmetrical fore and aft, while in the second case the aft end is curved to a fine point.

4. For the first case we take a spindle-shaped body which has been used for experimental work at the National Physical Laboratory; for this form the source distribution is

$$f(h) = a\{(h/l) - (h/l)^3\}; \quad -l < h < l. \quad (5)$$

The shape of the surface for this case has been given by Perring.\* It is sufficient to state here that it is a surface of revolution symmetrical about the middle cross-section and having pointed ends with finite angle of entrance; it can be made to have any required ratio of breadth to length.

We can, in this case, carry out the integration in (2) and obtain the equation of the longitudinal section. It is found that with  $2b$  as the breadth of the model,  $2l$  its length, and  $\delta$  the ratio of  $b$  to  $l$ , then the constant  $a$  of (5) is equal to  $\frac{1}{2}abc$ , where

$$\alpha = \delta/[4(1 + \delta^2)(10 + 9\delta^2) - \delta^2(1 + \frac{3}{4}\delta^2) \log(\delta/(1 + (1 + \delta^2)^{\frac{1}{2}}))]. \quad (6)$$

The equivalent distribution of doublets, given by the conditions stated in (3), is

$$\psi(h) = -\frac{1}{4}al(1 - h^2/l^2)^2. \quad (7)$$

Substituting in (4) we obtain the wave resistance

$$R = 4\pi g^4 \rho l^4 a^2 c^{-8} \int_0^{\pi/2} I^2 \sec^5 \phi e^{-(2gl/c^2) \sec^3 \phi} d\phi, \quad (8)$$

where

$$I = \int_0^1 (1 - u^2)^2 \cos(glu/c^2 \cos \phi) du. \quad (9)$$

After evaluating (9), the expression (8) can be reduced to standard form as

$$\begin{aligned} R = \frac{256\pi g \rho b^2 l \alpha^2}{p^3} \int_0^{\pi/2} & \left[ \cos \phi + \frac{12}{p^2} \cos^3 \phi + \frac{144}{p^4} \cos^5 \phi \right. \\ & - \left( \cos \phi - \frac{60}{p^2} \cos^3 \phi + \frac{144}{p^4} \cos^5 \phi \right) \cos(p \sec \phi) \\ & \left. + 12 \left( \frac{\cos^2 \phi}{p} - \frac{12 \cos^4 \phi}{p^3} \right) \sin(p \sec \phi) \right] e^{-\beta p \sec^2 \phi} d\phi, \end{aligned} \quad (10)$$

where  $\beta = f/l$ ,  $p = 2gl/c^2$ , and  $\alpha$  is given in (6).

An asymptotic expansion suitable for large values of  $p$  could be obtained, but calculation from it is very tedious; the particular point under consideration can be made by comparison with the similar expression for the second case.

\* W. G. A. Perring, 'Trans. Inst. Nav. Arch.', 1925.

5. For comparison we require a solid of revolution of which the front end is a sharp point of finite angle while the rear end is cut away to a point of zero angle; there will, of course, be a point of inflection in the curve of the rear portion.

This is obtained by taking the source distribution to be

$$f(h) = ah(2l - h)(3l + h)^2; \quad -3l < x < 2l. \quad (11)$$

The equivalent doublet distribution over the same range is

$$\psi(h) = -\frac{1}{3} a(2l - h)^2(3l + h)^3. \quad (12)$$

The outline of the model was found by the graphical methods described in § 2; the work is not reproduced here as it was only carried out with sufficient accuracy to verify that the curve was of the required type. A similar curve is shown later in fig. 1. The model has now a length  $5l$ , and it is not symmetrical fore and aft of the maximum cross-section.

From (4) we find the wave resistance

$$R = \frac{1}{2} \frac{\rho}{g} \pi g^4 \rho a^2 c^{-8} \int_0^{\pi/2} (I^2 + J^2) \sec^5 \phi e^{-(2g/c^2) \sec^2 \phi} d\phi, \quad (13)$$

where

$$I + iJ = \int_{-3l}^{2l} (2l - h)^2 (3l + h)^3 e^{ig h/c^2 \cos \phi} dh. \quad (14)$$

Evaluating (14) and substituting in (13), the terms can be collected in the same form as in (10); if we write, with  $2b$  as the maximum breadth of the model,

$$a = abc/125l^4, \quad p = 5gl/c^2, \quad \beta = 2f/5l, \quad (15)$$

we obtain ultimately

$$\begin{aligned} R = \frac{320\pi g \rho b^2 l \alpha^2}{p^3} \int_0^{\pi/2} & \left[ \cos \phi + \frac{18}{p^2} \cos^3 \phi + \frac{432}{p^4} \cos^5 \phi + \frac{7200}{p^6} \cos^7 \phi \right. \\ & + 6 \left( \frac{1}{p} \cos^2 \phi - \frac{128}{p^3} \cos^4 \phi + \frac{1200}{p^5} \cos^6 \phi \right) \sin(p \sec \phi) \\ & \left. - 6 \left( \frac{17}{p^2} \cos^3 \phi - \frac{528}{p^4} \cos^5 \phi + \frac{1200}{p^6} \cos^7 \phi \right) \cos(p \sec \phi) \right] e^{-\beta p \sec^2 \phi} d\phi. \end{aligned} \quad (16)$$

We may now compare (10) and (16) as regards the matter under discussion. We imagine the resistance graphed as a function of the velocity, and we compare the relative magnitude of the oscillations superposed upon the mean curve. The terms in (10) and (16) which give rise to these oscillations are the

terms factored by  $\sin(p \sec \phi)$  or  $\cos(p \sec \phi)$ . For large values of  $p$ , we have an asymptotic expansion of any of these terms in the form

$$\int_0^{\pi/2} \cos^n \phi \cdot e^{ip \sec \phi - \beta p \sec^2 \phi} d\phi \sim p^{-1/2} e^{ip} (a_0 + a_1 p^{-1} + a_2 p^{-2} + \dots). \quad (17)$$

Moreover, in practice, the interference effects concerned are prominent for larger values of  $p$ , say, for the range 10 to 40. Now from (10) we see that the expansion of the oscillatory terms would begin with a term of order  $p^{-1/2}$ , while from (16) the lowest term is of order  $p^{-3/2}$ . It follows, therefore, that the interference effects have been largely eliminated by the alteration made in the form of the model. It may be noted that the alteration is rather extreme if considered as an illustration of practical conditions, in that the after end of the model is cut away completely to zero angle; this accounts for the complete absence of the term in  $p^{-1/2}$  in the expression for the second case.

6. To examine the matter graphically, it is easier to consider a model of infinite draught, and of small ratio of beam to length, in the manner used in previous papers. The model is assumed to be symmetrical about a longitudinal vertical plane. Take  $Ox$  horizontally in this plane, and let  $Oy$  be also horizontal. The form of the horizontal cross-section of the model is constant; if its equation is

$$y = F(x), \quad (18)$$

for positive values of  $y$ , the approximation consists in taking the doublet distribution of (4) so that

$$2\pi \partial\psi/\partial x = c\partial F/\partial x. \quad (19)$$

Integrating (4) by parts with respect to  $h$  and  $h'$ , substituting from (19), and also integrating with respect to  $f$  and  $f'$ , we have

$$R = \frac{4\rho c^2}{\pi} \int \frac{\partial F}{\partial h} dh \int \frac{\partial F'}{\partial h'} dh' \int_0^{\pi/2} \cos \left\{ \frac{y(h-h')}{c^2} \sec \phi \right\} \cos \phi d\phi. \quad (20)$$

We wish to contrast two models which have the front half the same, but with the rear end smoothed off to a finer point in one case than in the other. We shall take the section of unsymmetrical form to be given by

$$y = (b/4l^3) (l-x)(2l+x)^2; \quad -2l < x < l. \quad (21)$$

For the symmetrical model we shall take the front portion to be given by (21) for  $x$  positive and by the corresponding expression for  $x$  negative. The model in one case is of length  $2l$  and in the other of length  $3l$ . The cross-sections by a horizontal plane are shown in fig. 1.

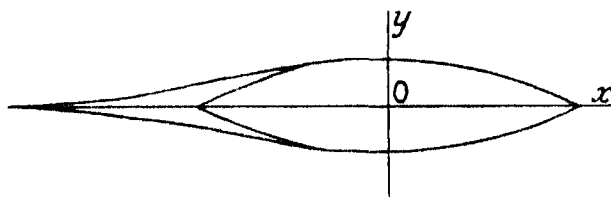


FIG. 1.

7. Taking the symmetrical case first, we obtain from (20),

$$R = 9\rho b^2 c^2 \pi^{-1} \int_0^{\pi/2} J^2 \cos \phi \, d\phi, \quad (22)$$

where

$$J = \int_0^1 (2u + u^2) \sin (glu/c^2 \cos \phi) \, du. \quad (23)$$

From these we have, after reduction, and writing  $p$  for  $2gl/c^2$ ,

$$\begin{aligned} R = \frac{324g\rho b^2 l}{\pi p^3} \left\{ \frac{2}{3} + \frac{128}{135} \frac{1}{p^2} + \frac{1024}{105} \frac{1}{p^4} + P_3(p) - \frac{16}{3} \frac{1}{p} P_4(p) \right. \\ \left. + \frac{112}{9} \frac{1}{p^2} P_5(p) + \frac{128}{9} \frac{1}{p^3} P_6(p) + \frac{64}{9} \frac{1}{p^4} P_7(p) - \frac{32}{3} \frac{1}{p^2} P_5(\frac{1}{2}p) \right. \\ \left. + \frac{256}{9} \frac{1}{p^3} P_6(\frac{1}{2}p) - \frac{256}{9} \frac{1}{p^4} P_7(\frac{1}{2}p) \right\}, \quad (24) \end{aligned}$$

with the notation

$$P_{2n}(p) = (-1)^n \int_0^{\pi/2} \cos^{2n} \phi \sin (p \sec \phi) \, d\phi,$$

$$P_{2n+1}(p) = (-1)^{n+1} \int_0^{\pi/2} \cos^{2n+1} \phi \cos (p \sec \phi) \, d\phi.$$

Using sequence relations for the  $P$  functions, we reduce (24) to a form involving only  $P_3$ ,  $P_4$  and  $P_5$ ; tabulated values of these have been given previously,\* and in addition large-scale graphs of the three functions were available over the range of  $p$  from zero to 40. These graphs have been used also in the present calculations; the reduced form of (24) from which these have been made is

$$\begin{aligned} R = \frac{324g\rho b^2 l}{\pi} \left\{ \frac{2}{3} + \frac{0.9482}{p^2} + \frac{9.752}{p^4} + \left( 1 + \frac{2.54}{p^2} \right) P_3(p) \right. \\ \left. - \left( \frac{5.333}{p} + \frac{11.684}{p^3} \right) P_4(p) + \left( \frac{14.984}{p^2} - \frac{6.1}{p^4} \right) P_5(p) \right. \\ \left. + \frac{2.2}{p} P_3(\frac{1}{2}p) - \frac{24.04}{p^3} P_4(\frac{1}{2}p) - \left( \frac{8.466}{p^2} - \frac{24.4}{p^4} \right) P_5(\frac{1}{2}p) \right\}. \quad (25) \end{aligned}$$

\* 'Roy. Soc. Proc.,' A, vol. 108, p. 82 (1925).

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The graph is shown in curve A of fig. 2, the base being  $c/\sqrt{(2gl)}$ .

8. For the unsymmetrical model of fig. 1, we have

$$R = (9\rho b^2 c^2 / 4\pi) \int_0^{\pi/2} (I^2 + J^2) \cos \phi \, d\phi, \quad (26)$$

where

$$I + iJ = \int_{-2}^1 (2u + u^2) e^{iqlu/c^2 \cos \phi} \, du. \quad (27)$$

In this case the reductions lead to,

$$R = \frac{2187g\rho b^2 l}{4\pi p^3} \left\{ \frac{2}{3} + \frac{64}{15} \frac{1}{p^2} + \frac{1152}{35} \frac{1}{p^4} - \frac{4}{p} P_4(p) - \frac{28}{p^2} P_5(p) - \frac{72}{p^3} P_6(p) - \frac{72}{p^4} P_7(p) \right\}, \quad (28)$$

where  $p$  is now  $3gl/c^2$ .

For purposes of calculation this is put in the form

$$R = \frac{2187g\rho b^2 l}{4\pi p^3} \left\{ \frac{2}{3} + \frac{64}{15} \frac{1}{p^2} + \frac{1152}{35} \frac{1}{p^4} - \frac{96}{7p^2} P_3(p) - \frac{4}{p} \left( 1 - \frac{102}{7p^2} \right) P_4(p) - \frac{4}{7p^2} \left( 73 - \frac{108}{p^2} \right) P_5(p) \right\}. \quad (29)$$

The graph of (29) is shown in curve B of fig. 2.

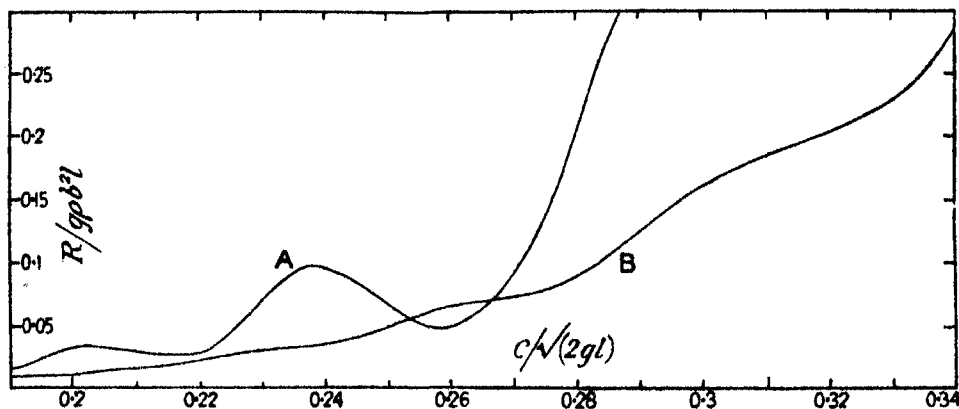


Fig. 2.

9. The curves for the two models are given with the same co-ordinates, namely,  $R/g\rho b^2 l$  and  $c/\sqrt{(2gl)}$ ; since the lengths of the models are different, the maxima and minima of the superposed oscillations occur at different speeds in the two cases.

The difference in the magnitude of the interference effects is sufficiently obvious from these curves. The variation in the form of the models shown in fig. 1 is considerable, and it would have been of interest to compare forms intermediate between those shown for the rear part of the model; but equations for such curves led to expressions for the wave resistance which were too complicated for numerical calculation. However, it may be inferred that for any case in which the lines of the model are smoothed out in this manner there will be a very considerable reduction in the magnitude of the interference effects.

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*On the Formation of Water Waves by Wind (Second Paper).*

By HAROLD JEFFREYS, M.A., D.Sc., F.R.S., Fellow and Lecturer of St. John's College, Cambridge.

(Received November 24, 1925.)

In a previous paper\* I investigated the problem of the formation of waves on deep water by wind, and found that the available data were consistent with the hypothesis that the growth of the waves is due principally to a systematic difference between the pressures of the air on the front and rear slopes. Lamb† had already discussed the maintenance of waves against viscosity by an approximate method, but without obtaining numerical results. Being under the incorrect impression that Lamb's approximation would not hold for the short waves I was chiefly considering, I proceeded on more elaborate lines. It now appears, however, that Lamb's method is not only applicable to the problem of waves on deep water, but is readily extended to cover the case when the water is comparatively shallow, and to allow for surface tension. The fundamental approximations are first, the usual one that squares of the displacements from the steady state can be neglected, and second, that viscosity modifies the motion of the water to only a small extent. The motion of the water can then, to a first approximation, be considered as irrotational.

With the previous notation, let  $\zeta$  be the elevation of the free surface,  $x, y, z$  the position co-ordinates,  $t$  the time,  $U$  the undisturbed velocity of the water,  $h$

\* 'Roy. Soc. Proc.,' A, vol. 107, pp. 189-206 (1925).

† 'Hydrodynamics,' §§ 349, 350.

the depth, and  $\phi$  the velocity potential. Also let  $\sigma$ ,  $p$ ,  $q$ , and  $\mathfrak{S}$  denote respectively  $\partial/\partial t$ ,  $\partial/\partial x$ ,  $\partial/\partial y$ , and  $\partial/\partial z$ , and write

$$p^2 + q^2 = -r^2. \quad (1)$$

Further, let the ratio of surface tension to density be  $T'$ . Then the velocity potential satisfies Laplace's equation

$$(\mathfrak{S}^2 - r^2) \phi = 0, \quad (2)$$

whence

$$\phi = Ux + e^{rz}A + e^{-rz}B \quad (3)$$

where  $A$  and  $B$  are independent of  $z$ . At the free surface we have

$$w = \mathfrak{S}\phi = r(A - B), \quad (4)$$

and also

$$\frac{d\zeta}{dt} = (\sigma + Up)\zeta. \quad (5)$$

At the bottom  $z = -h$ , and  $w = 0$ . Hence

$$e^{-rh}A - e^{rh}B = 0, \quad (6)$$

and

$$\phi = Ux + \frac{\sigma + Up}{r} \frac{\cosh r(z + h)}{\sinh rh} \zeta. \quad (7)$$

The disturbance of pressure at the surface  $z = 0$  is  $g(\rho - \rho')\zeta + \rho T' r^2 \zeta$ , allowing for the weight of the air displaced, but not for the disturbance of its velocity. It is also equal to  $-\rho(\sigma + Up)(\phi - Ux)$ .

Hence

$$\left[ \frac{(\sigma + Up)^2}{r} \coth rh + g \frac{\rho - \rho'}{\rho} + T' r^2 \right] \zeta = 0. \quad (8)$$

Suppose now that the water is initially at rest, so that  $U = 0$ , and assume that

$$\zeta = a \cos(\gamma t - \kappa x) \cos \kappa' y. \quad (9)$$

Then

$$\phi = -\frac{\gamma a}{r} \frac{\cosh r(z + h)}{\sinh rh} \sin(\gamma t - \kappa x) \cos \kappa' y, \quad (10)$$

where now

$$r^2 = \kappa^2 + \kappa'^2. \quad (11)$$

The kinetic energy of the water is given by

$$2T = \rho \iint \phi \frac{\partial \phi}{\partial n} dS \quad (12)$$

taken over the bounding surfaces,  $dn$  being an element of the outward normal.

The mean kinetic energy of a column of the water, of unit cross section, if  $\kappa'$  is not zero, is then evidently

$$\frac{1}{8}\rho \frac{\gamma^2 a^2}{r} \coth rh, \quad (13)$$

since  $\partial\phi/\partial n$  is zero at the bottom. The gravitational potential energy is  $\frac{1}{2}g(\rho - \rho') \zeta^2$  per unit area, and its mean value is  $\frac{1}{8}g(\rho - \rho') a^2$ . The potential energy due to the extension of the surface is  $\frac{1}{2}\rho T' [(p\zeta)^2 + (q\zeta)^2]$ , and its mean value is  $\frac{1}{8}\rho T' r^2 a^2$ . The mean potential energy per unit area is therefore  $\frac{1}{8}a^2 [g(\rho - \rho') + \rho T' r^2]$ , which, by (8), is equal to the mean kinetic energy. The total energy per unit area is therefore

$$E = \frac{1}{4}\rho \frac{\gamma^2 a^2}{r} \coth rh. \quad (14)$$

The rate of dissipation of energy is

$$\mu \iint \frac{\partial Q^2}{\partial n} dS \quad (15)$$

where  $\mu$  is the mechanical viscosity, otherwise denoted by  $\nu\rho$ , and  $Q$  is the resultant velocity. Now

$$Q^2 = (p\phi)^2 + (q\phi)^2 + (\nabla\phi)^2, \quad (16)$$

and its mean value at a given depth is found, after some simplification, to be

$$Q^2 = \frac{\gamma^2 a^2}{4 \sinh^2 rh} \cosh 2r(z+h). \quad (17)$$

The mean value of  $\partial Q^2/\partial n$  at the bottom is zero. At the surface

$$\left(\frac{\partial Q^2}{\partial n}\right)_{\text{mean}} = r\gamma^2 a^2 \coth rh. \quad (18)$$

The rate of dissipation in a column of unit cross section is therefore equal, on an average, to

$$\mu r \gamma^2 a^2 \coth rh. \quad (19)$$

Now suppose the wind to have velocity  $V$ , and call the wave velocity  $c$ . Then

$$c = \gamma/\kappa. \quad (20)$$

The velocity of the wind relative to the crests is  $V - c$ , and if  $s$  be the sheltering coefficient\* the part of the pressure of the air that contributes to wave growth is  $s\rho' (V - c)^2 p\zeta$ . The rate at which the pressure does work per unit

\* Jeffreys, *loc. cit.*, p. 193.



area is equal to the product of the pressure and the downward normal velocity. Thus it is equal to

$$s\rho'[(V-c)^2 p\zeta][-\sigma\zeta] = s\rho'(V-c)^2 \gamma \kappa a^2 \sin^2(\gamma t - \kappa x) \cos^2 \kappa' y,$$

and its mean value is

$$\frac{1}{4} s\rho'(V-c)^2 \gamma \kappa a^2. \quad (21)$$

From (14) and (19), the energy, in the absence of wind, satisfies the equation

$$\frac{d}{dt} \left( \frac{1}{4} \rho \frac{\gamma^2 a^2}{r} \coth rh \right) = -\mu r \gamma^2 a^2 \coth rh, \quad (22)$$

and hence  $a$  varies like  $\exp(-2\nu r^2 t)$ . The only effect of the three-dimensional character of the wave is then to replace  $\kappa$  by  $r$ . If  $\kappa'$  were zero the mean value of  $\cos^2 \kappa' y$  would be 1 instead of  $\frac{1}{2}$ , but this affects all the quantities concerned and the growth or decay of waves involves only their ratios. Neither finiteness of depth nor surface tension affects the rate of decay.

From (19) and (21) we see that the wave will grow if

$$\frac{1}{4} s\rho'(V-c)^2 \gamma \kappa > \nu \rho r \gamma^2 \coth rh, \quad (23)$$

which may be written

$$\frac{(V-c)^2}{c} > \frac{4\nu \rho}{s\rho' \tanh rh} \frac{r}{\kappa^2}. \quad (24)$$

We recall that, by (8),

$$c^2 = \left[ g \frac{\rho - \rho'}{\rho} + T'r^2 \right] \frac{r}{\kappa^2} \tanh rh. \quad (25)$$

Now if  $V$  is given the left side of (24) increases steadily as  $c$  diminishes, and therefore has its greatest value when  $c$  is a minimum. The right side increases steadily with  $r$ , and therefore, subject to  $\kappa$  being the same, is an increasing function of  $\kappa'$ . By (25),  $c$  is also an increasing function of  $\kappa'$  if  $\kappa$  is kept constant. Hence if  $\kappa'$  is not zero, we can increase the left side of (24) and decrease the right side by decreasing  $\kappa'$ . The inequality (24) therefore has the best chance of being satisfied if  $\kappa' = 0$ . Thus the easiest waves to excite are always two-dimensional.

Taking now  $\kappa' = 0$ , (25) becomes

$$c^2 = \left[ \frac{g}{\kappa} \frac{\rho - \rho'}{\rho} + T'\kappa \right] \tanh \kappa h, \quad (26)$$

whence

$$2c \frac{dc}{d\kappa} = \left[ -\frac{g}{\kappa^2} \frac{\rho - \rho'}{\rho} + T' \right] \tanh \kappa h + \left[ \frac{g}{\kappa} \frac{\rho - \rho'}{\rho} + T'\kappa \right] h \operatorname{sech}^2 \kappa h. \quad (27)$$

When  $\kappa$  is zero, this is negative ; when  $\kappa$  is infinite, it is positive ; and, indeed, when  $\kappa$  is such that

$$\frac{g}{\kappa^2} \frac{\rho - \rho'}{\rho} = T', \quad (28)$$

$2c (dc/d\kappa)$  is positive. Thus there is always a minimum velocity, and the corresponding wave-length is greater than that which gives the minimum velocity on deep water. The minimum velocity is evidently less than the minimum velocity on deep water.

If now  $\kappa$  is such that the wave-length is less than that which corresponds to the minimum wave velocity, we see that, as  $\kappa$  decreases,  $c$  decreases, and therefore  $(V - c)^2/c$  increases. At the same time  $\kappa/\tanh \kappa h$  decreases. Thus the inequality (24), if satisfied by any value of  $\kappa$  in this range, will be satisfied by the value giving the minimum velocity. The easiest wave to excite is therefore never a ripple, in the Kelvin sense.

We are therefore limited to gravity waves in two dimensions. Now the depth enters (24) and (25) only through  $\tanh \kappa h$ , which is practically unity if  $\kappa h > 1.5$ , and practically  $\kappa h$  if  $\kappa h < 0.5$ . The former case is that of deep water, which was examined in the previous paper. If indeed we ignore  $T'$  and put  $\tanh \kappa h = 1$ ,

$$c^2 = \frac{g}{\kappa} \frac{\rho - \rho'}{\rho}$$

and

$$\kappa c = \frac{g}{c} \frac{\rho - \rho'}{\rho}.$$

Then (24) becomes

$$(V - c)^2 c > \frac{4\nu g (\rho - \rho')}{s\rho'}, \quad (29)$$

which is identical with equation 3 (14) of the previous paper. This was there found to imply that the easiest wave-length to excite was about 8 cm., based on the observational fact that waves first appear when  $V$  is about 110 cm./sec., and itself agreeing with observation so far as yet tested. Then  $\kappa = 0.7/1$  cm. nearly, and then if  $\kappa h = 1.5$  we must have  $h = 2$  cm. nearly. The former theory should, then, hold for water of all depths greater than about 2 cm. The critical wave-length is great enough for the neglect of surface tension to be justifiable.

Taking now the other extreme case, where  $\tanh \kappa h$  is replaceable by  $\kappa h$ , we find that (24) and (25) reduce to

$$\frac{(V - c)^2}{c} > \frac{4\nu\rho}{s\rho'h}, \quad (30)$$

$$c^2 = (g + T'\kappa^2)h, \quad (31)$$

where the unimportant factor  $(\rho - \rho')/\rho$  has now been dropped. The right side of (30) is now a constant, and the easiest wave-length to excite, therefore, corresponds to the smallest wave-velocity. This is evidently  $\sqrt{gh}$ , provided the wave-length is several times  $2\pi\sqrt{T'/g}$  or 1.8 cm. Then

$$\{V - (gh)^{\frac{1}{2}}\}^2 > \frac{4\nu\rho}{s\rho'} \left(\frac{g}{h}\right)^{\frac{1}{2}}. \quad (32)$$

Thus the velocity needed to raise waves is determinate. But this analysis is only valid if  $\kappa h < 0.5$ , which for a wave-length of 1.8 cm. would make  $h < 0.14$  cm.; actually, with longer waves, it may be several times greater. But a further restriction is operative. The minimum velocity is less, and the corresponding wave-length greater, than are applicable in deep water. On both grounds the period is greater; the period corresponding to the least velocity on deep water is about 0.08 sec. Now viscosity is dominant through a region whose thickness is about the square root of the product of the kinematic viscosity and the period, or, with these values, 0.038 cm. The conditions of shallow water will increase this result several times, and further viscosity will be operative both at the top and the bottom, thus again doubling the thickness affected. Thus in long waves on shallow water the motion will be dominated by viscosity, and no wave-formation will be possible. The only waves capable of being formed, therefore, are those whose length is not great enough to make the shallow-water approximation valid; the easiest waves to form have, therefore, lengths not more than about four times the depth. This agrees with what is observable in shallow roadside puddles. When the wind is strong enough to raise considerable waves on deep water, it often produces no noticeable disturbance in these puddles; a strong wind will raise waves, but their length does not exceed about 2 cm. It is easily found from (24) that waves of this length would be formed on deep water by a wind of 160 cm./sec., and this would hold for depths down to about 1 cm.

### *Summary.*

On the hypothesis that, in a first approximation, water waves may be considered irrotational, viscosity and other factors tending to change the amplitude being small, it has been found possible to investigate the conditions of growth of waves under the action of wind, even when the depth is finite and surface tension is allowed for. It is found that the rate of decay of waves, in the absence of wind, is independent of the depth and the surface-tension. The easiest waves for a wind to raise are always two-dimensional, and are

gravity waves, not ripples. The wind velocity needed to produce waves is greater in shallow water than in deep water. The longer waves on shallow water (less than about 1 cm. deep) are, however, so much affected by viscosity that the hypothesis that viscosity exerts only a modifying effect on the motion is invalid for them, and it seems that they can in no case be formed by wind. The waves produced on shallow water must therefore be very short, about 2-3 cm. say, which agrees with observation.

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*The Excitation of Soft X-Rays.*

By O. W. RICHARDSON, F.R.S., Yarrow Research Professor of the Royal Society, and F. C. CHALKLIN, B.Sc., King's College, London.

(Received September 14, 1925.)

§ 1. In a paper (1) by one of us (O. W. R.) and Prof. Bazzoni it was shown that it was possible to detect the excitation of characteristic soft X-rays, such as the K X-rays of carbon, by a photoelectric method. The substance under investigation was bombarded with electrons in a highly-evacuated bulb of quartz glass, and the radiation generated, after passing between two parallel plates of a vacuum condenser to filter out ions and electrons, was received on a metal plate from which the photoelectric emission could be measured. The photoelectric current increases with the thermionic electron current, and with the potential difference driving the latter. If the photoelectric current divided by the thermionic current is plotted against this potential difference the excitation of characteristic X-rays setting in at certain voltages could be detected by the existence of discontinuous changes of slope in the curves so obtained. Similar observations were made almost simultaneously by A. I. Hughes (2), E. H. Kurth (3), P. Holweck (4), and Mohler and Foote (5), and since that time a very considerable number of papers on this subject has appeared (6) — (16).

This paper gives an account of measurements made since the autumn of 1923 on the elements carbon, tungsten, nickel and iron, starting with carbon and proceeding in the order named. It is believed that they represent a progressive improvement in this branch of experimenting so that the accuracy of the results probably increases from carbon to iron. It should also be made clear that the present communication does not represent an immediate continuation

of the work done with Prof. Bazzoni and referred to above. There was an intervening period (1921–1923) in which some experiments were made by one of us (O. W. R.) with the collaboration of Prof. U. Yoshida and later of Dr. H. H. Potter. The experiments made with Prof. Yoshida, on carbon and nickel, showed that the photoelectric current due to the general radiation, divided by the primary thermionic electron current, as measured in our apparatus, was nearly proportional to the voltage driving the primary electron current over the range 0–600 volts. Apart from this, which was quite definite, some of the other results obtained seemed rather indecisive, and they were not published as it seemed, at the time, that publication might tend to retard rather than to advance progress. A considerable number of the measurements with carbon included in the present paper were made with the collaboration of Dr. Potter.

The apparatus in its present form is shown to scale in plan in fig. 1. The

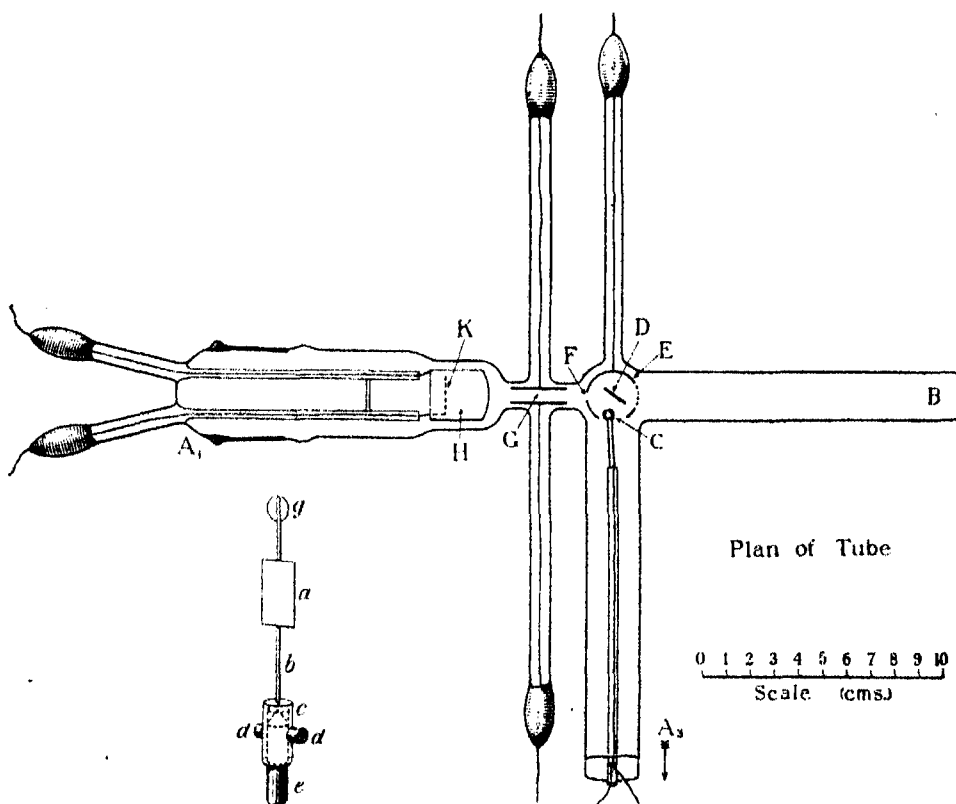


Fig. 1.

container is of transparent quartz glass made by the Thermal Syndicate, Wallsend-on-Tyne, and, except for the stoppers supporting H, D and C, is a single piece. The outlet B is connected through two wide double-walled glass condensers in series, one containing coconut charcoal, which are normally immersed in liquid air, to a fast mercury pump backed by a box oil pump and a Geryk oil pump in succession. The joints and seals are all made with a minimum quantity of hard sealing wax, which is quite satisfactory owing to the low vapour pressure of this cement. They are all a long way from the central heated parts of the apparatus, and remain quite cold owing to the low thermal conductivity of quartz. Lead seals were used in the earlier apparatus, but appear to be unnecessary, and are inconvenient. Tests with the apparatus arranged as an ionisation manometer show that pressures of  $10^{-8}$  mm. may be maintained under working conditions. There is no particular difficulty about maintaining pressures in the neighbourhood of  $10^{-7}$  mm., and effects due to gas radiation do not in general become appreciable unless  $10^{-6}$  mm. pressure is exceeded. It will be shown that with soft X-rays, as with hard, anticathodes of higher atomic number are more efficient emitters than those of lower atomic number under a given primary voltage. The proportion of the total radiation under given conditions arising from a given amount of gas is thus greatest for targets of the lightest elements. It is also relatively greater at the lower voltages. For carbon at 100 volts the radiation from residual gas at  $10^{-6}$  mm. pressure contributes, in this apparatus, about 10 per cent. of the total measured photoelectric effect.

The cathode of the X-ray tube consists of a few turns of 2 ampere tungsten wire wound in a cylindrical spiral of which C is a circular section. The anticathode D is a rectangular plate 1 cm. wide and 2 cm. high whose thickness varied somewhat for the different materials. These electrodes were surrounded by a cylindrical copper screen E 4 cm. high with a vertical slit at F 0.28 cm. wide and 1.84 cm. high and other openings as indicated. The screen is supported by the quartz walls. The metal condenser plates G, which trap the ions and electrons out of the beam of radiation emerging through the slit F, are held tight against the flat walls of the quartz container which is here of rectangular section. They are respectively  $2.25 \times 1.85$  cm. and  $2.35 \times 1.94$  cm. and vary from 0.54 to 0.56 cm. apart. The radiation emerging from them falls on the copper plate K surrounded by the copper box H, which is open in front. The photoelectric electron emission from K is measured by a suitable electrometer.

In all the experiments with carbon, nickel and tungsten the photoelectric

measurements were made by taking the time of the electrometer spot over a given section of the scale. It is difficult to get the accuracy required to elucidate the finer points of the phenomena by this method, and in the experiments with iron a constant deflection method in which the adjoining quadrants were shunted with an alcohol-xylol resistance was substituted.

When the X-ray generating part of the apparatus is working, and the pressure is of the order  $10^{-6}$  mm. or less the plate K will generally charge up positively, even if there is no potential difference between the condenser plates G. This is caused by the photoelectric effect of the X-radiation (the photoelectric effect of the radiation from the filament is negligible under our working conditions) augmented by the positive ions and diminished by the negative ions and electrons diffusing out of the X-ray tube. Either of the two latter effects may exceed the other depending on the relative potentials of the surfaces C, D, E and the two plates of G; so that the deflection may be either greater or less than that due to the true photoelectric effect of the X-radiation. If now a potential difference is applied across the condenser plates G, these ions or electrons will be attracted to the plates, and the current in the photoelectric chamber will be diminished or increased according to whether diffusion of positive ions was predominating over that of negatively charged particles or the contrary. If this potential difference is sufficiently increased all the ions and electrons will be removed from the stream of radiation, and any further increase will not affect the current in the photoelectric chamber. Fig. 2 shows one of numerous tests of this kind. The photoelectric currents as

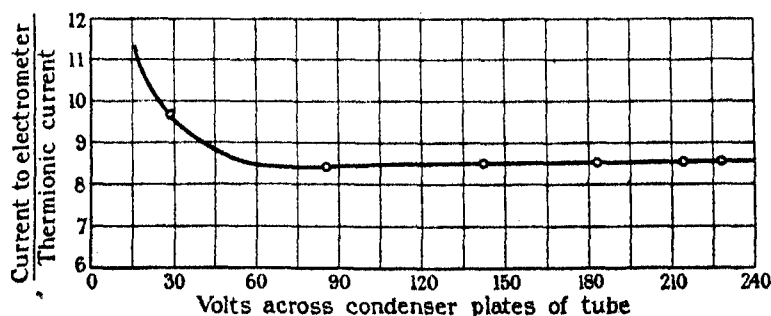


FIG. 2.

ordinates are plotted against the potential difference between the condenser plates as abscissæ. In this case the current fell at first showing that the diffusion of positively charged particles was predominant. The current, however, remains practically constant as soon as about 100 volts is exceeded. In

this test the voltage on the X-ray tube was about 230. It is essential to work on the flat part of fig. 2 for every voltage applied to the target. The results of a test showing the satisfaction of this condition, with a carbon target, is shown in fig. 3. In this case the potential on the condenser plates is varied between about 280 and 300 volts with successive target voltages of 50, 100, 200, 300, 400, 500 and 600. At each target voltage the current is independent of the field between the condenser plates over the limits used. Fig. 3 is of further interest because it shows the excitation of the K radiation of carbon. It will be noticed that the photoelectric effect increases by equal steps for equal increments in target voltage from 50 to 300 volts, but above 300 volts the rate of increase is much greater. This is due to the excitation of the K X-rays from carbon which sets in at about 290 volts. It is essential in working the apparatus that sufficient voltage should be applied between the condenser plates to extract all the ions and electrons from the beam, and this condition should be ascertained by tests of the kind indicated.

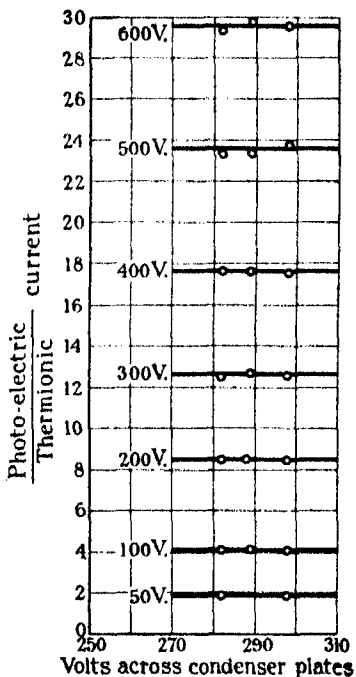


FIG. 3.

Provided this condition is satisfied, it is found that with a constant voltage on the target the photoelectric current due to the radiation is proportional to the primary electron current in the X-ray tube. This does not distinguish between the effect of radiation coming from the target and that due to residual gas. The additional effect due to gas has been examined separately by Yoshida with the result that with a given voltage on the target it is proportional to the pressure of the gas over the range from  $10^{-7}$  to  $10^{-5}$  mm. It is also for a given pressure nearly proportional to the primary electron current, and nearly independent of the voltage driving the latter, provided this is not allowed to become unreasonably high, in which case if there is any appreciable quantity of gas in the apparatus the results tend to become erratic. The magnitude of the radiation from residual gas at  $10^{-5}$  mm. pressure is about equal to that from a solid carbon surface at a voltage of 100 with the same primary current. The relative magnitudes of the radiation from the gas and from the solid under other



conditions can be deduced from the foregoing statements and the discussion in § 6 below.

When allowance is made for the effect of gas if it is necessary, and the resulting photoelectric current due to the solid is divided by the primary electron current, the resulting fraction is found to be nearly proportional to the primary voltage for each of the four solids here investigated. The linear relation is, however, disturbed by the occurrence of irregularities such as changes of slope generally attributed to the excitation of characteristic radiation. These may not necessarily be due to the element of which the target is believed to be composed, but may be due to contaminants. This would be analogous to the occurrence of lines due to impurities in ordinary spectra. It is also rather probable that as the primary voltage is increased, the distribution of the electron current density over the surface of the target will change. It is possible that such changes in the incidence of the primary current on the target might give rise to changes in the photoelectric effect considered as a function of the primary voltage similar in character to those caused by the appearance of characteristic rays. Such spurious effects should be independent of the material of the target, but would presumably be affected by changes in the geometry and potentials of the essential metal parts of the X-ray tube and of the condenser plates. Changes of slope which are similar in character and set in at the same voltage for a number of different substances should therefore be regarded as suspicious. If they are of the spurious kind last referred to, they should occur at different voltages with different types of apparatus and possibly with changes in the electrical conditions of the tube. If they are due to impurities they should always occur at the same voltage, but might vary in intensity or disappear with changes in the conditions. It may be some time before we have sufficient knowledge of this spectral region to eradicate such effects properly. For this and other reasons we regard all the results of the present paper as only provisional in character.

In preparing the tubes the central part round E.G.H. is first thoroughly heated with a blow-pipe and with the pumps running. This gets most of the gas out of the metal parts. The remainder is got out by bombarding the target to incandescence with a heavy electron current from the filament at 3000 to 4000 volts, the shield being connected to the filament. This is carried out, with the usual precaution to prevent damage to the filament, until no more gas is evolved. In the more recent work the target has been mounted on a pivoted brass tube with an iron arm so that it could be turned with a magnet from outside. With this arrangement the bombardment can be carried out

with one side facing the tungsten spiral and the X-ray tests made with the other side facing the spiral. In this way the danger of the results being vitiated by the presence of impurities volatilised out of the tungsten should be greatly reduced.

## § 2. Carbon.

The broad features of the X-ray emission from carbon bombarded by electrons with energies up to 600 volts are shown by the two graphs *a* and *b*, in fig. 4.

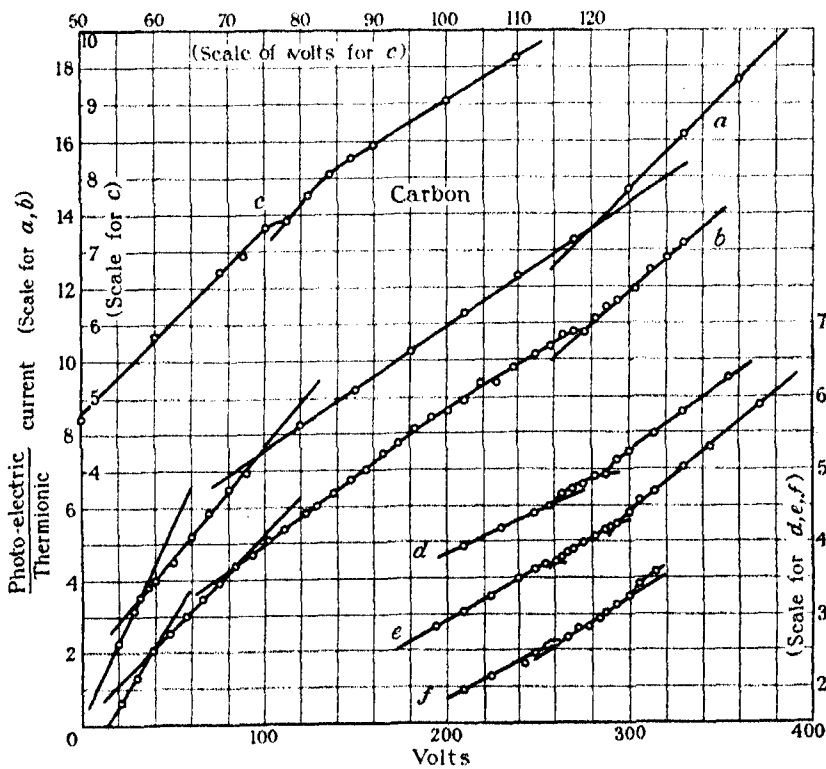


FIG. 4.

In this and similar figures the ordinates are actual ratios of the currents expressed in convenient units, but these units are not in general the same for different figures. The absolute values of the ratios are considered in Section 6 below. Fig. 4*a* is arbitrarily displaced upwards by two units on the vertical scale for clearness. Actually the observations plotted only extend to 360 volts, but separate tests gave no inflections between 360 and 620 volts. These curves are taken with a wide interval—5, 10, or 15 volts—between the readings so

as to cover the whole range whilst the apparatus is working satisfactorily. Owing to the wide spacing of the points some detail is apt to be lost, and these curves are not particularly useful for determining the points of inflection with accuracy. We took seven sets of readings of this type and they all showed the same features, consisting of four straight, or almost straight, lines intersecting at about 40, 80, and 280 volts. The inflections near 40 and 80 volts were downward. A downward inflection does not prove that the point is not an X-ray excitation potential, as Brainin (17) has shown that the excitation of the K X-rays in a silver anti-cathode is characterized by a downward inflection of this type. The three other elements investigated all have inflections near both 40 and 80 volts. Of those near 80 volts, the tungsten one is downwards, the nickel one upwards, and the iron one either upwards or downwards. That of tungsten is most similar to that of carbon in character, but it seems to be at too low a voltage to be the same phenomenon. The evidence, in fact, seems to be against this inflection being an instrumental property of the apparatus. There is also some extraneous support for it. Mohler and Foote (5) have recorded a sharp inflection with  $C_2H_2$  at 75 volts approximately. McLennan and Clark (7) refer to preliminary observations of distinct discontinuities at 72 volts. These authors all used quite distinct types of apparatus from ours. The results, uncorrected, of a detailed investigation of this point are shown in fig. 4c. Six such tests were carried out, and each of them gave the kind of dimple shown in the figure. This seems to suggest that the actual discontinuity at the point may be an upward inflection.

The inflection near 280 volts is due to the excitation of the K X-rays from carbon. A detailed examination of this region has shown indications of some fine structure on the low-voltage side of it. Three sets of readings on successive days gave the results shown in fig. 4, *d*, *e*, *f*, where only curve *d* has the correct ordinates, *e* and *f* being depressed one and two units respectively so as to keep the points distinct. It will be seen that there are very clear indications of an inflection at about 290 and another at about 30 volts lower. It is possible, however, that the lower inflection may be due to tungsten.

The inflection near 40 volts also appears to be complex. About a dozen experiments in which the readings were taken one volt apart gave results of the type shown in fig. 5, curves *a* and *b*. These kinks are so close together that it is difficult to locate them with sufficient accuracy with our apparatus in its present form, so that they appear to wander about a little in the different experiments. It is unlikely, however, that they are not real, although it is very easy to get small fluctuations of this type when the apparatus is not

working quite satisfactorily. Unless the points are taken very close together the curves appear as intersecting straight lines, as shown in curve *c* of fig. 5.

The potentials shown in figs. 2-5, and in similar figures throughout the paper, are those read directly from the voltmeter placed across the gap between the hot cathode and the target. It is necessary to consider what corrections have to be made to these in order to find the voltage which is equivalent to the work to be done on an electron by the time it has penetrated the surface of the target. This voltage, presumably, will determine the maximum frequency of the emitted radiation in accordance with the relation  $eV = w = h\nu$ . These corrections have generally been considered but there seem to be some errors or omissions in all the accounts we have seen.

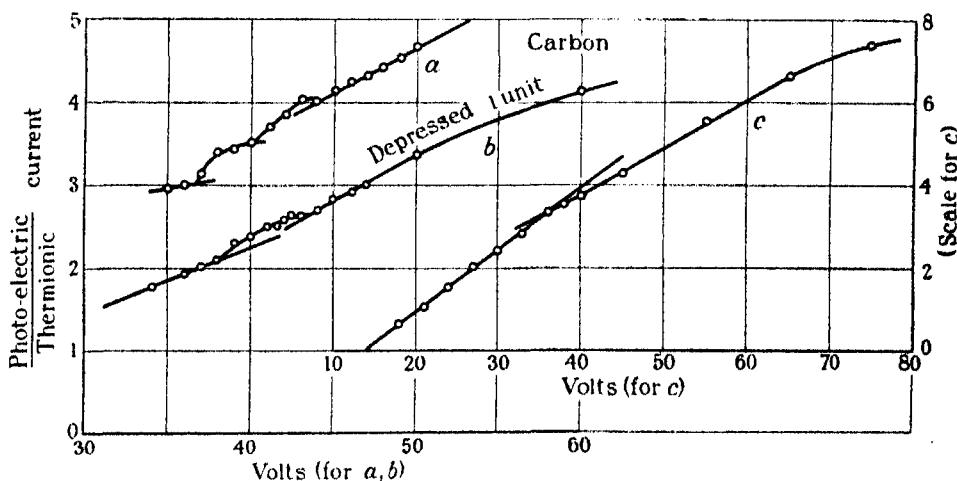


FIG. 5.

One obvious and important correction is for the drop in potential in the hot cathode due to the flow of the current through it; so that the potential shall be measured from the part of the cathode from which the electrons first emerge in appreciable quantities. With a hot-wire cathode the ends are much cooler than the middle, and practically all the electrons come from the hottest part. An equipotential source is, of course, very desirable if high resolving power is to be attained. We sacrificed this to some extent, and used a rather long filament in order to get a sufficient emission at a low enough temperature for the filament to last a long time, and also to avoid evaporation of the matter of the filament on to the cathode. From observation we concluded that the middle third of our cathode was fairly uniform in temperature and hotter than the ends. The

drop along this section of it was about 2 volts. We have made this correction by subtracting one-third of the total drop down the filament, since the voltmeter was connected to the negative end of it. If the connection is to the positive end of the filament the correction involves the addition of two-thirds of the drop. Possibly about 0.5 volt of this correction may be a matter of uncertainty. As a result of experience, we believe that the length of the filament could, if necessary, be reduced considerably, with a similar increase in the sharpness of the resulting data.

An addition has to be made for the initial emission velocity of the electrons. As this is distributed according to Maxwell's law, the velocity of an individual electron can have any value between 0 and  $\infty$ , so that this correction lacks definiteness. However, the proportion of the electrons whose energy deviates from the mean by any considerable multiple is small, so that we shall take the average as sufficient. This is  $V = 2kT/e$  or 0.391 volt at 2000° C.

The other matters for which it is necessary to make a correction are the work done on an electron when it enters the target, and the work done on it by the contact potential difference  $K$  between the hot cathode and the target. These quantities are, of course, not registered by the voltmeter. If the target is a simple substance with a single threshold  $\phi_0$ , the work done on an electron on entering the target is  $\phi_0$  and the equivalent potential difference  $\phi_0/e$ . The total addition to the voltmeter reading for these two corrections is thus  $K + \phi_0/e$ . This is identically equal, neglecting a small thermoelectric term, to  $\phi'_0/e$ , where  $\phi'_0$  is the work function of the material of the hot cathode (also assumed to be a simple substance with one threshold). If we add the preceding correction for the emission velocities to these two, we get altogether  $1/e (\phi'_0 + 2kT)$ , which is a very simple quantity, namely, the voltage equivalent of the latent heat of evaporation of electrons *from the hot cathode* (not the target) at its temperature during the experiment. This quantity is accurately known, especially owing to the measurements of Davisson and Germer. Its value at any absolute temperature  $T$  is  $1/e (\phi'_0 + 2kT) = 4.5 + 0.0001675 T$  volts, or 4.88 volts at 2270° K. This value is almost certainly correct to within two or three units in the second decimal place. If the target is a simple substance with one threshold but the cathode is a material, such as a dull emitter, with more than one threshold and is working at a low temperature, so that only the lowest threshold is operative in the thermionic emission, then we have to use the value of  $1/e (\phi'_0 + 2kT)$  for the low threshold which is actually operative. This quantity can be deduced from measurements of the saturation current  $i$  from the hot cathode at different temperatures by means of the relation

$i = AT^2e^{-\phi_0/kT}$ . This paragraph is rather condensed, but the details can be found from the following references: O. W. Richardson, 'Phil. Mag.', vol. 23, p. 263 (1912); Richardson and Cooke, *ibid.*, vol. 21, p. 410 (1911); Davisson and Germer, 'Phys. Rev.', vol. 20, p. 300 (1922); Richardson, 'R.S. Proc.,' A, vol. 105, p. 387 (1924); Richardson and Young, *ibid.*, vol. 107, p. 377 (1925). Throughout the present paper, after making the correction for the potential drop in the filament, 4.9 volts have been added on account of the three other corrections.

In this paper we disregard the fine structure which appears to be involved in the inflection near 40 volts and treat it as a single level. So treated 14 measurements gave the following values for the voltage at the point of inflection after applying the correction for the fall of potential down the filament only:—34.0, 32.86, 35.30, 34.56, 34.7, 33.5, 34.7, 35.3, 34.3, 35.4, 34.9, 33.5, 34.3, 36.1. The average of these is 34.6 volts. We also obtained the following values from three long range curves with the readings a considerable distance apart:—32, 32, 36.5, mean 33.5. Excluding these the final corrected value is  $34.6 + 4.9 = 39.5$  volts.

For the inflection near 80 volts there are 15 determinations with the following values:—75.1, 75.0, 74.5, 71.5, 77.0, 77.0, 77.0, 75.5, 79.7, 74.6, 75.3, 76.4, 79.1, 78.4, 75.9, mean = 76.3 volts. In addition there are three values 84.9, 77.7 and 78.7, mean 80.4, obtained with an older apparatus which differed from the other mainly in that the cylindrical shield was reduced to a curved plate about 2 cm. across with a slit in it immediately in front of the condenser plates. With this apparatus this inflection was upwards not downwards. It is difficult to judge whether this behaviour should be regarded as increasing the probability of its being a characteristic X-ray point or not. It appears that this inflection was looked for carefully by Levi (13) without success. Presumably if it can sometimes bend down and at other times up it can also be absent. There are also 7 long range determinations 77.5, 83.5, 75.5, 77.8, 81.3, 85.1, 90.6, mean = 81.6. If we disregard the last 10 values as being probably less accurate than the first 15 the final value is  $76.3 + 4.9 = 81.2$  volts.

For the point near 280 volts we have the following 7 values, 290.2, 292.0, 294.1, 286.0, 286.9, 280.3, 286.3, mean 287.9. There are also 8 values taken from long range curves with points wide apart, viz.:—294, 287, 282.9, 275.8, 285, 286, 280.8, 287.6, mean 284.9. If we disregard these as less accurate the final value is  $287.9 + 4.9 = 292.8$  volts.

For the point on the low voltage side of the last there are 5 determinations,

viz.:—256, 262, 259, 262·1, 261·2, mean 260·1. The final value is thus  $260·1 + 4·9 = 265·0$  volts.

The final values turned into wave-lengths are :

Volts .. ..	39·5 (7)	81·2 (7)	265·0 (2)	292·8 (10)
Å ..	312·5	152·0	46·6	42·2
$\nu/R$ ..	2·92	5·99	19·55	21·62

There is some slight difficulty in comparing these values with those given by other experimenters, especially in the lower voltage regions, since most of the authors say very little about how they applied the corrections discussed above. For the K excitation potential the following values have been published :—Richardson and Bazzoni (1) 286, Holtsmark (6) 287·5; Kurth (3) 289·4; Levi (13) 293·0. These compare with the present value of 292·8 volts. The inflection at 265 volts compares with one given as 259 by MacLennan and Clark (7). For the L excitation potential we have Hughes (2), 34·5; Kurth (3) 32·9; McLennan and Clark 33·0 (7); Levi (13) 35·0. Our value is appreciably higher than these at 39·5 volts. Millikan's interpretation of the spectrum of carbon in the Lyman region requires that the excitation potential for the L spectra should exceed 34·2 volts. The difference  $292·8 - 39·5 = 253·3$  is not very far from the inflection at 265 volts, which, if it is really a carbon inflection, presumably represents the result of some process by which an electron can be temporarily transferred from the K level to an orbit whose energy is comparable with that of the orbits in the L level. A possible interpretation of the inflection at 81·2 volts is to attribute it to a double ionisation of the L level.

### § 3. Tungsten.

The specimen of tungsten was a sheet  $1·9 \times 1·0 \times 0·1$  cm<sup>3</sup>. placed as nearly as possible in the same position as the removed carbon specimen. The case of tungsten is of technical interest because in using a tungsten cathode the other targets will become sputtered over with this substance, and one would expect that in time the various targets would begin to give effects characteristic of tungsten. Up to the present we do not appear to have been troubled much by this effect, but that may be because we have taken precautions to avoid it as far as possible.

The broad features over the range 40 to 600 volts are shown in 3 sections in fig. 6, where the curve consists of intersecting straight lines with a downward inflection near 70, upward inflections near 180, 250 and 350, and a downward

inflection near 410 volts. (The vertical scales are different for figs. 6a, 6b and 6c.) Below 40 volts there is a weak downward bend which in reality

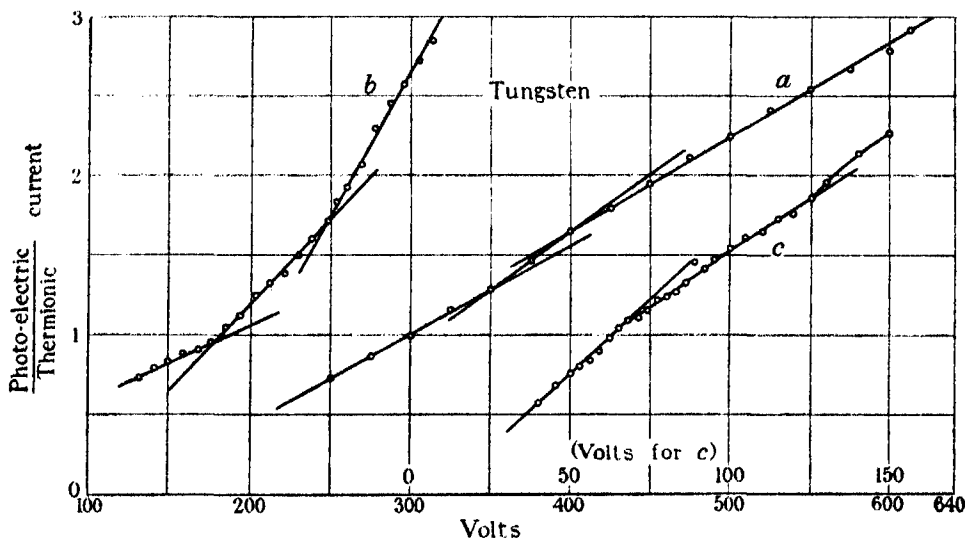


FIG. 6.

appears to consist of 3 components as shown by the observations plotted in fig. 7a. When the voltage interval between the observations is shortened there are indications of something abnormal near 125 and near 145 volts. The details of these as well as of the inflections near 70 and 180 volts are shown in fig. 7b-f. The vertical scale unit has been arbitrarily altered in fig. 7b and c, and the values are all raised by 0.2 in fig. 7f. The discontinuity at about 145 volts is weak, and that at 125 volts appears to be double, as also does the one near 250 volts. The details of this are shown in fig. 8, curve a. The region between 330 and 430 volts is difficult to interpret in detail, partly owing to the large amount of general radiation. The impression we have of it is that it consists of a strong upward break at 330 to 340 volts, and two weaker breaks at about 390 and 420 volts. The inflection at 330 volts is shown in unusual strength in fig. 8, curve b, and the phenomena near 400 volts in fig. 8, curves c and d. The ordinates for c are raised 2 units to separate the curves.

For the weak triple inflection between 30 and 40 volts we have the following values:—For the lowest break, 32.4, 31.4, 33.3 and 30.65, mean = 31.94 volts. There are also 3 less accurate values for this point which, however, would not alter the mean if taken in. For the next point which is relatively weak there is one accurate measurement which puts it at 35.4 volts, and two



others which may be considered as confirming this. For the third point which is intermediate in strength there are two accurate measures which agree in placing it at 40.0 volts. When the corrections other than for the filament drop are added the final values are :—36.84 (6), 40.3 (1), 44.9 (3) volts. The figures in brackets are attempts to guess at the relative intensities.

There are four measures of the downward inflection near 70 volts, viz. :—65.7, 62.7, 66.6, 68.6, mean, 65.9. The final corrected value is thus 65.9 +

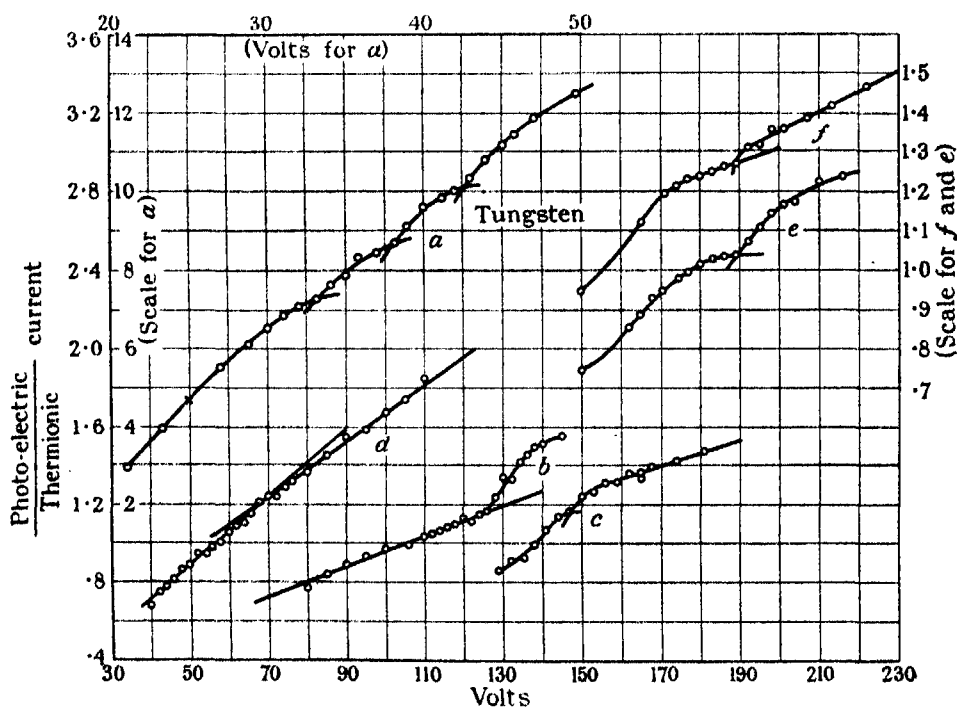


Fig. 7.

$4.9 = 70.8$ . This break is very similar in appearance to the one found with carbon at 81.2 volts, but it is very improbable that they can be the same thing, since the difference between 81.2 and 70.8 is too great.

The next two inflections are not very strong, and have little effect on the general inclination of the graphs. The one at about 145 volts is weaker than the one near 125, and the latter shows indications of a weak component at about 108 volts. For this faint component we have two identical measures each giving  $103.3 + 4.9 = 108.2$  volts. For the inflection near 125 we have five measures, viz. :—123.3, 122.8, 122.9, 122.7, 122.3, mean = 122.8, with a

final value  $122.8 + 4.9 = 127.7$  volts. For the inflection near 145 we have four good values, viz. :—145.8, 141.8, 147.2, 145.2, mean = 145 volts. There are also three others not so definite which average 1.4 volts less. If we disregard them the final value is  $145 + 4.9 =$  say 150 volts.

For the inflection in the neighbourhood of 180 we have the following measures :—190.3, 186.6, 186.8, 185.5, 177.7, 186.8, mean, 185.6. There are also eight others, which if included would raise the average about 0.5 volt.

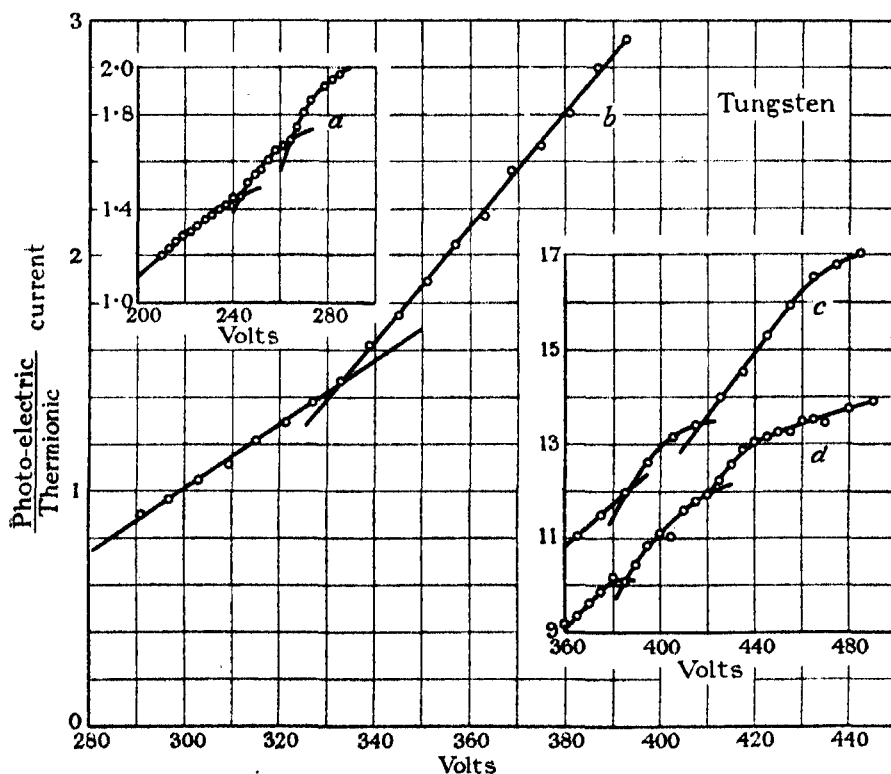


FIG. 8.

We therefore take the final value to be  $185.6 + 0.5 + 4.9 = 191$  volts. On one occasion only this inflection is shown as distinctly double, with components at  $191 \pm 12$ , but it seems difficult to interpret this otherwise than as an accidental experimental error.

For the inflection near 240 we have two measures, 240.8 and 239.8, mean 240.3, giving a final value  $240.3 + 4.9 = 245.2$  volts. For the inflection near 260 we have also 2 measures, 261.8, 255.8, mean, 258.8, giving a final value

263.7. In addition if we include graphs in which these two points are unresolved we have for the composite level 246.8, 242.8, 248.8, 237.8, 251, 244, mean, 245.1, giving a final value 250. This lies well within the limits of the proposed components.

For the inflection near 330 our measures are 331, 328, 327, 339, 328, 328, 334, mean 331. There are also two others not so good at 340 and 328. If we disregard these the final value is  $331 + 4.9 =$  say, 336. For the point near 390 we have the following measures, of which the first two appear to be the best:—394, 388, 392, 393, 384, 386, 388, 393, mean 390, giving a final value, say, 395. There are also two long range curves, of which fig. 6, curve *a*, is one, which show a single inflection between 300 and 400 at 351 and 363 respectively. These are taken to be  $336 + 395$  unresolved. Near 410 we have the following measures, of which the two first again appear to be the best:—409, 413, 410, 415, 419, 413, 419, mean 414, giving a final value 419 volts.

The final data are collected together in the following table, the figures in brackets being attempts to guess the relative intensities of the inflections.

Table II.

Volts .....	36.84 (5)	40.3 (0)	44.9 (2)	70.8 (7)	108.2 (0)	127.7 (2)	150.0 (1)
A .....	335.0	306.5	275.0	174.3	113.9	96.7	82.3
$\nu/R$ .....	2.72	2.975	3.315	5.23	7.98	9.41	11.07
.. (B & C) .....	2.5	2.9	—	5.2	—	—	—
.. (H) .....	2.5	2.7	—	—	—	—	—
.. (C) .....	3.0-3.2	—	—	—	—	—	—
.. (N) .....	2.9, 2.8	—	—	5.2	5.7	—	—
	$N_{VI}$ $N_{VII}$	$O_{II}$ $O_{III}$	—	$O_{II}$ $O_{III}$	$O_I$	—	—

Volts .....	191 (8 to 4)	245.2 (4)	263.7 (4)	336 (10 to 5)	395.0 (2)	419.0 (2)
A .....	64.6	48.6	46.8	36.75	31.25	29.5
$\nu/R$ .....	14.10	18.10	19.45	24.80	29.16	30.95
.. (B & C) .....	—	17.8	18.7	—	—	30.6
.. (H) .....	—	17.6	—	—	—	—
.. (C) .....	—	18.5	18.4	—	—	30.9
.. (N) .....	—	18.4	18.8	—	—	33.0
	—	$N_V$	$N_{IV}$	—	—	$N_{III}$

Measurements of inflections for tungsten have been published by Bazzoni and Chu (10), and by Boyce (12). Bazzoni and Chu found an inflection having indications of a complex structure between 33 and 40 volts, and another break at 71-72 volts. Inflections were found by Boyce at 32.8, 37.2, 74, 360, 403, 583 and 815 volts. Except that 74 is rather high these values, if allowance is made for some difference in the method of applying the corrections, are in agreement with our observations if they are interpreted as 32.8 (= 36.84),

37.2 ( $= 40.3 + 44.92$  unresolved), 74 ( $= 70.8$ ), 360 ( $= 336 + 395$  unresolved), 403 ( $= 395 + 419$  unresolved). We should not expect to detect Boyce's inflection at 583 as it is too near the end of our voltage limit to make its appearance on a long range curve, and we have not made a detailed examination of this region. The point at 815 was beyond the limit of our battery.

Many of the measured values agree with X-ray energy levels, deduced by the application of the combination principle to X-ray measurements. This can be seen from the table where the third row gives the values of  $v/R$ , which correspond to the volts found in the present measurements and the fourth, fifth, sixth and seventh rows give the values of  $v/R$  assigned to the various levels of Bohr and Coster (18), Hjalmar (19), Cork, and Nishina (20) respectively. The values assigned to Cork are taken from the paper by Boyce (12) as we have not been able to find Cork's paper. If we take Nishina's tables, which are the most recent, as representing the position of the levels as deduced from X-ray measurements and the combination principle, the following are identical to within the combined limits of error of the two methods:—N VII (2.72, 2.8), N VI (2.975, 2.9), O II III (5.23, 5.2) N V (18.10, 18.4), N IV (19.45, 18.8), N III (30.95, 33.0). The only missing level within the range is O I (5.7). This is very close to O II, III (5.2) and may not have been resolved. On re-examining our data in this region we find that they are not accurate enough to conclude that it is absent. To attempt to interpret the seven additional inflections at this stage would be merely guessing. Possibly some represent cases of multiple ionization. Others may be due to impurities or instrumental properties. The strength of several suggests that they are not all due to impurities. The reality of 336 and/or 395 is strengthened by the fact that Boyce (12) with a quite different type of apparatus finds an inflection at 360, which is what we also find when our readings are taken too far apart to resolve this region completely. For other alternative possibilities reference may be made to § 7 below.

#### § 4. Nickel.

The target, also  $1.0 \times 1.9$  cm.<sup>2</sup>, was cut out of sheet nickel 0.021 cm. thick and mounted like the others except that it was strengthened by bending back the edges. Otherwise it was found to have a tendency to sag under bombardment. A general idea of the effects obtained over the range 40–400 volts is shown in fig. 9. From curve *a* it appears that in the range from 60 to 100 volts the curve shows three intersections at about 75, 86 and 97 volts. Between 100 and 400 volts the plot has some curvature over most

of its course, but with distinct intersections at about 140, 240, 280 and 310 volts. Between 360 and 600 the plot is also slightly curved and intersections are found at about 430 and 530 volts. Below this range there is an inflection at about 35 volts. This appears very variable in character as is shown in figs. 9c<sub>1</sub>-c<sub>5</sub>, where the five curves were taken in succession in the order in which they are numbered. It consists of two intersecting straight lines with

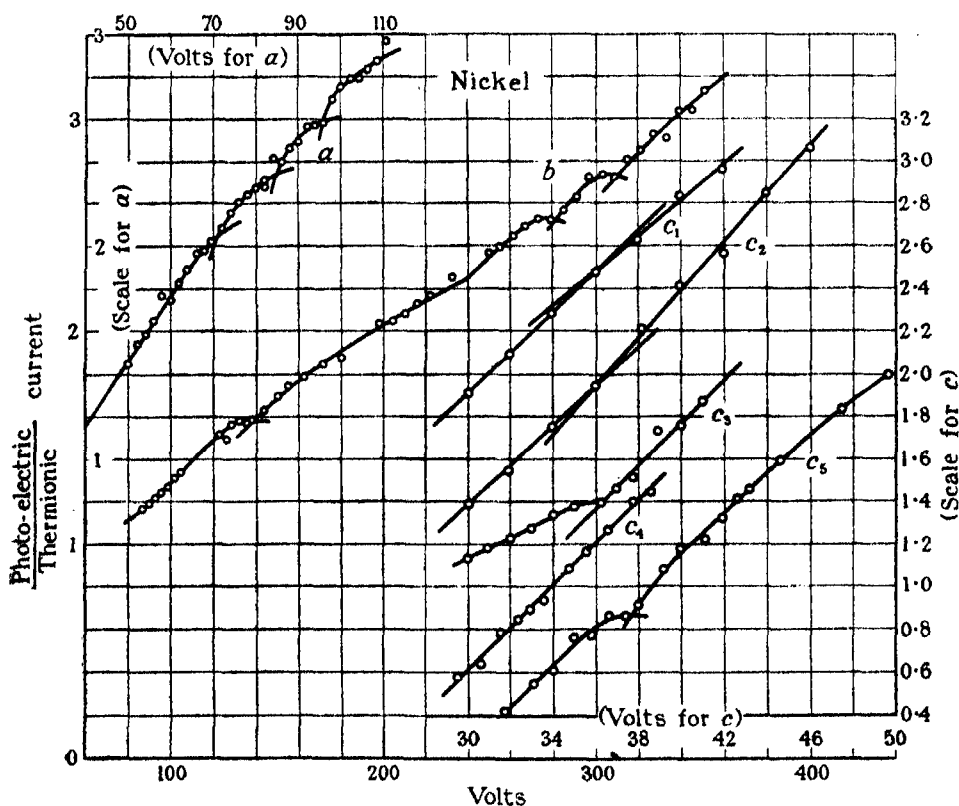


FIG. 9.

a downward bend in  $c_1$  and an upward bend in  $c_2$ . In  $c_4$  there is only a single straight line and the inflection has disappeared. In  $c_3$  the upward bend is quite pronounced, and there is a distinct curvature on the lower part. In  $c_5$  there is practically no bending, but there is a dimple at the former point of inflection. The ordinates of  $c_1$ - $c_5$  have been raised 0.6, 0.0, 0.6, -0.8 and -1.2 unit respectively in order from  $c_1$  to  $c_5$ . In addition to the points mentioned numerous curves have been obtained with inflections at about

330 and 390 volts. It seems possible that these together with the inflection at about 430 are due to tungsten. The detailed measurements are as follows :—

38·6. There are 9 measures of which 3 are disregarded as being comparatively rough, leaving 32·5, 32·5, 33·5, 33·6, 35·3, 34·9. Mean 33·7. This  $+ 4·9 = 38·6$  volts.

80·0. There are 4 measures, of which 1 is derived from indistinct data leaving 73·7, 74·9, 76·8. Mean 75·1. This  $+ 4·9 = 80·0$  volts.

88·9. There are 4 measures 83·2, 85·4, 84·1, 83·1. Mean 84·0. This  $+ 4·9 = 88·9$  volts.

99·0. There are 4 measures of which 1 is too rough, leaving 94·6, 93·6, 94·2. Mean 94·1. This  $+ 4·9 = 99·0$  volts.

140·3. There are 6 measures of which we retain 136·3, 136·3, 136·8, 132. Mean 135·4. This  $+ 4·9 = 140·3$  volts.

245·5. There are 9 measures, of which we retain 238·3, 240·3, 244·2, 238·4, 243·3, 247·3, 238·5, 234·5. Mean 240·6. This  $+ 4·9 = 245·5$  volts.

282. This is very near a strong inflection at 288. It only shows on 2 curves and must be regarded as weak and uncertain. On one curve it and the line 288 are both quite sharp and 6 volts apart. It is thus determined by subtracting 6 volts from the next inflection.

288. There are 13 measures, of which we disregard 5, leaving 278·3, 283·3, 280·3, 288·0, 289·3, 281·3, 282·3, 281·2. Mean 283·0. This  $+ 4·9 =$  say 288 volts.

316·4. There are 8 measures, of which we retain the following 7 :—307·3, 313·5, 316·3, 307·3, 316·3, 312·3, 307·2. Mean 311·5. This  $+ 4·9 = 316·4$  volts.

335. This can be seen on 8 curves, of which the 6 best give 331·5, 325·3, 331·3, 334·3, 331·3, 328·3. Mean 330·3. This  $+ 4·9 =$  say 335 volts.

392·4. This can be seen on 5 curves, giving 382·3, 386·4, 393·3, 387·2, 388·2. Mean 387·5. This  $+ 4·9 = 392·4$  volts.

433. This can be seen on 7 curves, but it is weak. A weighted mean of 7 estimations which range from 416 to 438 volts gives when finally corrected 433 volts.

532. There are 8 measures of this, viz., 532·2, 532·3, 520·3, 528·5, 518·5, 528·5, 534·3, 521·3. Mean 527. This  $+ 4·9 =$  say 532 volts.

These data, together with rough guesses at the relative intensities (in parentheses) and the corresponding quantities in Angström units and in  $\sqrt{R}$  are assembled in Table III.

Table III.

Volts.....	38.6 (3 to 0)	80.0 (3 to 1)	88.9 (6)	99.0 (6)	140.3 (4)	245.5 (7)	282.0 (1)	288.0 (8)
Å.....	320.0	154.3	138.9	124.7	88.0	50.0	43.8	42.9
$\nu/R$ .....	2.85	5.91	6.57	7.32	10.38	18.15	20.83	21.28
$\sqrt{\nu/R}$ .....	1.088	2.431	2.565	2.71	3.22	4.26	4.56	4.61

Volts.....	316.4 (7)	335.0 (7)	392.4 (2)	433.0 (2)	532.0 (5)
Å.....	39.0	36.9	31.5	28.5	23.2
$\nu/R$ .....	23.39	24.77	29.0	32.0	39.4
$\sqrt{\nu/R}$ .....	4.83	4.98	5.39	5.66	6.28

Other experimenters have published the following points of inflection for nickel in volts: 53.6 Levi (13), 76.8 Levi (13), 80.0 Mohler and Foote (5), 102.8 Levi (13), 104 Horton, Andrewes and Davies (8), 118 Holtsmark (6), 178 Horton, Andrewes and Davies (8), 245 Holtsmark (6), 355.1 Levi (13), 781.3 Levi (13). Of these 76.8 and 80.0 would appear to be the same as our 80.0, 102.8 and 104 the same as 99.0, 245 the same as our 245.5. 355.1 might be  $335 + 392.4$  unresolved and 781.3 is beyond our limit. Unless there is a remarkable numerical coincidence the values at 335 (7), 392.4 (2) and 433 (2) are due to tungsten, the tungsten inflections found in this region being at 336 (5 to 10), 395 (2) and 419 (2). In order to get the gas out of the anode at these high voltages it had to be heavily bombarded, and no doubt there was some tungsten sputtered on it. The point at 532 volts might also be due to tungsten, as we never made a detailed examination of the region between 500 and 600 volts with this element. Boyce gives an inflection of tungsten at 583 volts. There are also uncertainties about the origins of some of the other points. Three of them, namely, 38.6 (3 to 0), 80.0 (3 to 1), 288 (8), are practically coincident with the three strong carbon inflections at 39.5 (7), 81.2 (7) and 292.8 (10). This may be a coincidence, but it seems suspicious. It might also account for the variability of the first two members. If all the inflections are taken out as to the origin of which there might be ground for suspicion, we are left only with 88.9 (6), 99.0 (6), 140.3 (4), 245.5 (7) and 316.4 (7), 282 (1) being too weak to be considered as certain. Of these, only 99.0 has been observed with a different type of apparatus. Holtsmark has also observed 245.5, but his apparatus is very similar to ours. According to the results of the discussion given by Horton, Andrewes and Davies (8) any of the inflections 80.0, 88.9, 99.0 might lie within the limits for the M II-M III levels of nickel and 140.3 within the limits set for the M I level, so far as they are known at

present. How the other discontinuities should be interpreted there seems to be no precise indication at present. (See, however, the discussion at the end of § 5.)

### § 5. *Iron.*

Two important improvements in the apparatus have been introduced into the experiments with this element. The target *a*, fig. 1, is mounted on a vertical rod *b* screwed on to a hollow cylinder *c* on the same axis. The end of this cylinder rests on a pivot, being the pointed end of a circular rod *e* round which the inside surface of the cylinder *c* fits smoothly, *i.e.*, it can slide without appreciable friction, but does not shake. The iron studs *dd* enable the cylinder and target to be rotated from outside the apparatus by means of a magnet. The mirror *g* attached to the rod *b*, with its plane face parallel to the plane front of the target, enables the setting of the latter to be determined conveniently by means of a lamp and scale outside the tube. With this device one face of the target can be turned towards the hot cathode when it is being denuded of gas by electron bombardment from the latter; the target can then be rotated through  $180^\circ$ , so that the other surface faces the hot cathode when the measurements are being taken. In this way the trouble due to deposition of matter from the hot cathode on to the working face of the target is avoided, and it is probable that the deposition at the lower cathode temperatures used during the actual measurements is relatively innocuous.

The second improvement consisted in substituting a high-resistance leakage across the quadrants of the electrometer for the timing methods hitherto employed. This provided a steady deflection method of measuring the photo-electric currents. The resistance consisted of a U-shaped capillary tube filled with a mixture of one part alcohol and eight parts xylol. When a suitable resistance had been obtained the electrodes were sealed into the tube which was then sealed off. The tube used had actually a resistance of about  $10^{11}$  ohms. The area of the face of the iron target used was  $1 \times 1.9$  cm.<sup>2</sup>.

The general features from 240 to 600 volts are shown in fig. 10, curve *a*. There is a weak upward bend about 265, a strong one about 285 and a second weak one about 500 volts. The appearance of these when the points are taken closer together is shown in fig. 10, curves *b*, *c* and *d*. The shoulder above 285 might possibly be interpreted as a series of inflections. A general view of the region between 120 and 220 volts is shown in fig. 11*a*. There is a downward inflection near 130 and an upward one near 190 volts. The region between these two has not yet been examined in detail. The region between 50 and



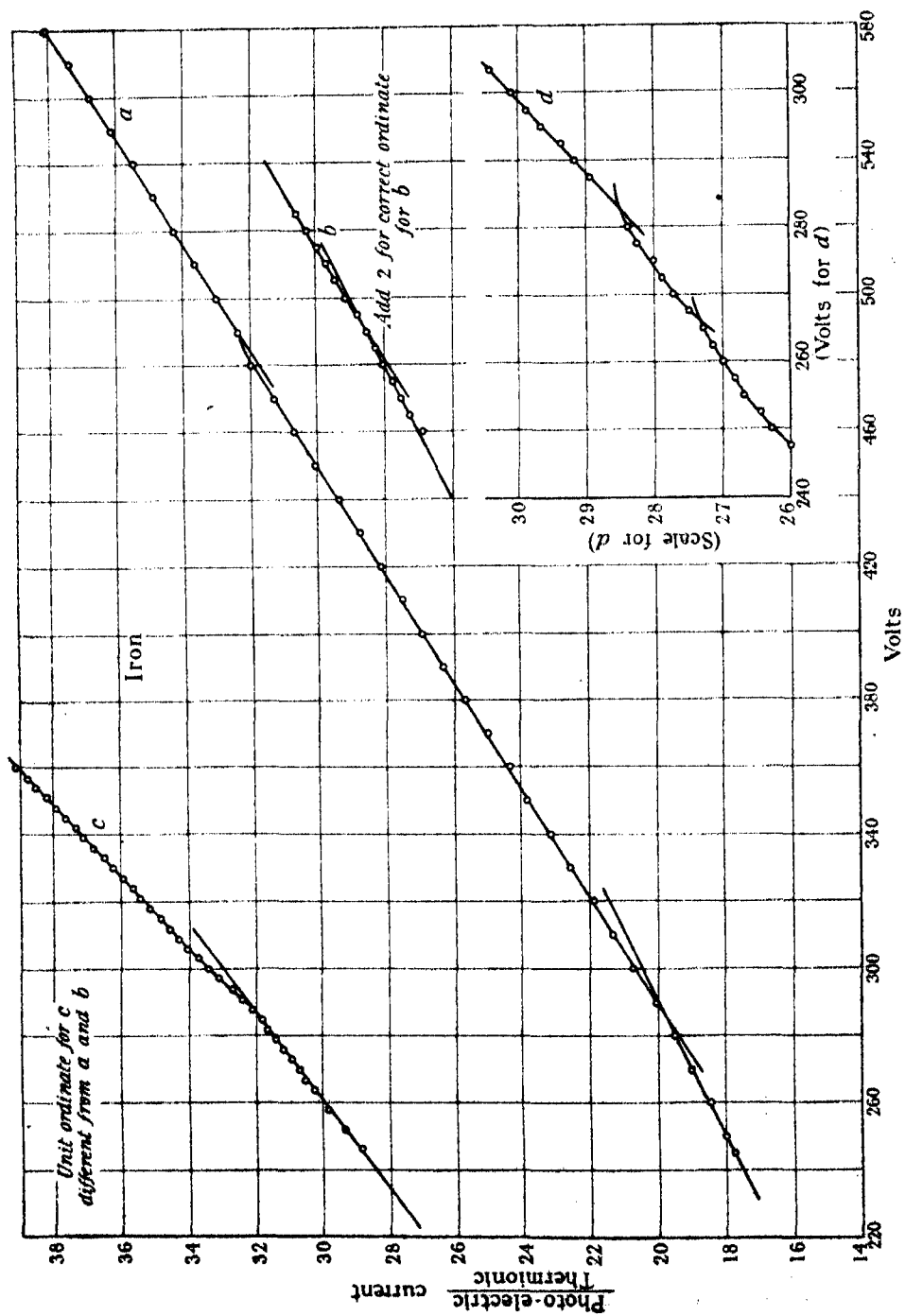


FIG. 10.

120 volts is shown in fig. 11, curve *b*. Some other curves show weak inflections above 95 volts, which do not appear on this one. There are two downward inflections at about 60 and 78, and an upward one at about 92 volts. Fig. 11, curve *c*, shows the appearance from 38 to 60 volts. There are two downward inflections, one at about 41 and one at about 47 volts. Many of these breaks

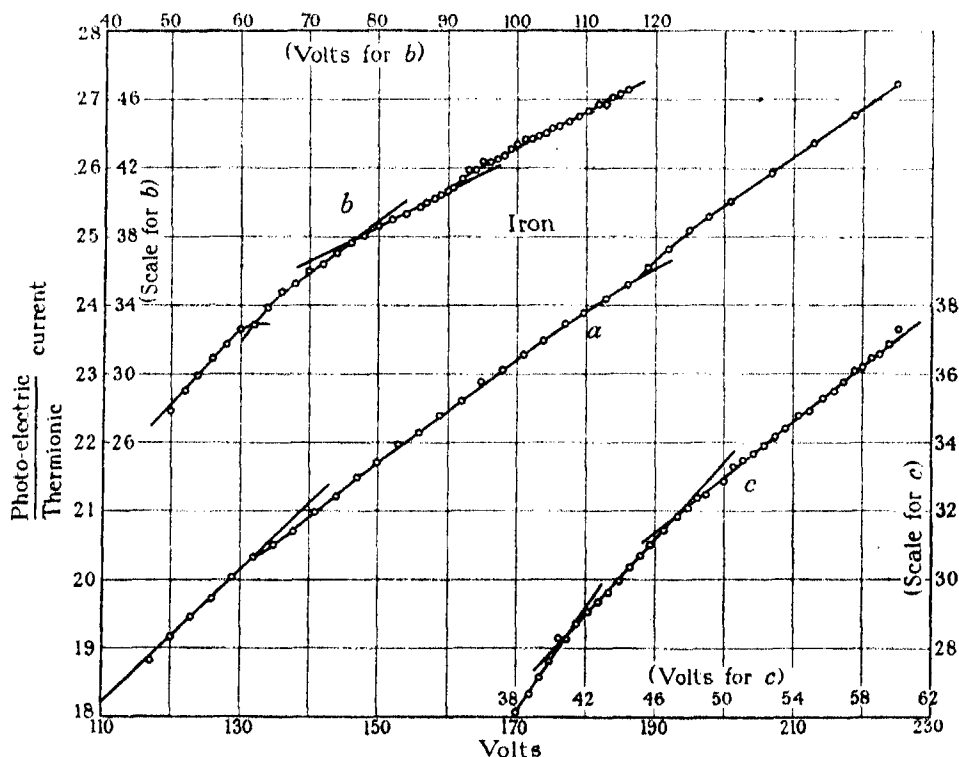


FIG. 11.

may be either upwards or downwards in different curves. The detailed measurements are as follows (the final correction  $+4.9$  volts is here omitted from the details):—

45.6 volts. 9 values, of which 1 is rejected, leaving 40.7, 41.6, 42.1, 40.8, 39.2, 38.2, 41.4, 41.3. Mean 40.7.

50.6 volts. 9 values, of which 1 is rejected, leaving 47.0, 44.7, 47.4, 45.1, 44.8, 44.6, 47.9, 44.4. Mean 45.7.

63.7 volts. 14 values 61.1, 58.4, 56.3, 58.8, 60.9, 58.4, 59.1, 57.9, 59.0, 57.2, 59.5, 58.6, 56.5, 61.2. Mean 58.8.

75.6 volts. 6 values, of which 1, 75.9 shown in fig. 16, Curve 1, is rejected

as unresolved from the next higher inflection, leaving 71.4, 69.8, 73.9, 68.1, 70.3. Mean 70.7.

84.8 volts. 6 measures, of which 1 is rejected, leaving 80.9, 80.8, 80.5, 76.8, 80.4. Mean 79.9.

95.0 volts. 8 measures, of which 2 are rejected as rough, leaving 89.9, 89.4, 90.8, 89.9, 90.4, 90.4. Mean 90.1.

107.6 volts. 6 measures, of which 1 is rejected as rough, leaving 101.9, 104.3, 102.8, 101.3, 103.4. Mean 102.7.

115.1 volts. 7 measures, of which 2 are rejected as indistinct, leaving 111.5, 108.3, 107.3, 112.1, 111.6. Mean 110.2.

137.6 volts. 10 measures, of which 1 is rejected as indistinct, leaving 132.4, 130.0, 133.3, 133.2, 133.2, 133.1, 134.0, 132.5, 132.7. Mean 132.7.

189.7 volts. 10 measures, of which 2 are unsatisfactory, leaving 184.1, 186.5, 183.0, 186.0, 181.2, 187.3, 183.3, 187.1. Mean 184.8.

221.5 volts. 4 sets of data, of which 1 is indefinite, leaving 215.4, 214.3, 220.1. Mean 216.6.

240.6 volts. 3 observations, of which 2 are retained, 235.8, 235.6. Mean 235.7.

270.2 volts. 3 observations, of which 1 is rough, leaving 265.9, 264.6. Mean 265.3.

288.3 volts. There are 18 measures of this, of which 2 are rejected as rough, leaving 284.9, 279.1, 281.8, 283.2, 278.3, 279.8, 284.1, 283.0, 285.1, 286.3, 284.8, 287.3, 284.4, 285.3, 283.6, 283.6. Mean 283.4.

498 volts. This point is difficult to locate with precision. There are 8 values, 483, 486, 484, 493, 493, 506, 495, 504. Mean 493.

In addition to the foregoing there may be some weak inflections between 120 and 180 volts, as this region has not yet been examined with sufficient thoroughness.

The most surprising thing about the inflections found with iron is the large number of them, and it does not appear that many of them can be attributed to any contaminants whose inflections are known. The strongest inflection found 288.3 (10) might be the carbon K excitation potential 292.8 (10). This is supported by the fact that there is something in the neighbourhood of each of the other two strong carbon inflections, 81.2 (7) and 39.5 (7), but it seems surprising that the strongest iron inflection should be due to an impurity. However, carbon is a likely impurity in iron, and we have not been able to secure a suitable piece of iron sheet with any guarantee as to chemical purity. Perhaps the best way of proceeding with the consideration of the matter is

to compare the values we have obtained with those published for this metal by other experimenters. These are shown in volts in the following table, the estimated relative intensities being given in brackets.

TABLE IV.

Our values	45.6 (3)	50.6 (3)			63.7 (4)	75.6 (2)	84.8 (2)	95.0 (3)
Thomas (15)	41.2 (2.5)	48 (2.4)	51.3 (1.6)	54.6 (3.1)	62 (2.7)	75.3 (2.2)	82.7 (2.3)	94.8 (1.3)
Rollefson (11)		46.8						
Kurth (3)			50				81.7	95.4
Horton et al. (8)						73		
Stuhlman (16)	45.8							
Our values	107.6 (0)	115.1 (1)	137.6 (6)					
Thomas	103.5 (2)	112.2 (1.7)	131.8 (1.9)				158.5 (1.7)	160.4 (2.3)
Rollefson		111.2	130.4	140.9	147.1	153.4	160.1	
Kurth								
Horton et al.								166
Stuhlman								
Our values		180.7 (6)	221.5 (2)		240.6 (1 to 3)		270.2 (2)	288.3 (10)
Thomas	181.6 (1.2)	192 (1.8)	221.3 (1.1)	228.1 (2.8)			277.4 (1.4)	288.6 (1.1)
Rollefson								
Kurth				227				
Horton et al.								
Stuhlman		200						
Our values			408 (2)					
Thomas	303.7 (1.8)	331 (1.6)			639 ? (0.9)	704.3 (1.5)		818.5 (2.0)
Rollefson				618	637	697		
Kurth							757	
Horton et al.								
Stuhlman								

In coming to a conclusion about the preceding table it should be recollected that our experiments only cover the range from 40 to 600 volts, and that our exploration of the stretch from 115 to 185 volts is only of a preliminary character and may not have taken in all the detail in that part. When this is borne in mind the agreement between our numbers and those of Thomas is quite convincing. It should be pointed out that all the values in Table IV except those at 84.8, 137.6 and 240.6 had been determined prior to the date at which Thomas' results were published. We feel that except for our inflection at 498 volts there is no substantial difference between the values found by Thomas and by us, except such as is a natural result of the experimental difficulties. The difference in the region 40-55 volts is due to the fact that the inflections are very close together. In fact the interpretation of this part is not very clear on the curves published by Thomas. The following points are the same to within the accuracy of the measurement: 63.7 (62), 75.6

(75.3), 84.8 (82.7), 95.0 (94.8), 107.6 (103.5), 115.1 (112.2), 189.7 (192), 221.5 (221.3), 288.3 (288.6). The point given by Thomas as 303.7 is entirely a matter of interpretation. Our curves show a downward bend here, but we interpreted it as a slowing down of the strong effect at 288.3. The same is possible of 228.1 in relation to 221.5 but the effect is not so clear. The difference between 270.2 (2) and 277.4 (1.4) may be due to some influence of tungsten contamination which has a fairly strong inflection at 263.7 (4). It is also possible that the inflections 240.6 (1 to 3) which we alone find, and 331 (1.6) which we do not find, are due to tungsten contamination. The tungsten inflections here are 245.2 (4) and 336 (10 to 5). It should be added that our "intensities" are rough attempts to express on a numerical scale the relative obviousness of the points of inflection whereas those given by Thomas are measurements of the ratio of the slopes of the graphs above and below the bend.

Whatever the interpretation of all these inflections may be it seems clear from a comparison of the numbers got independently by Thomas and by ourselves that the great majority of them are real. The possibility of inflections due to instrumental properties would appear to be almost excluded as the entirely different design of the tubes used would preclude their coincidence in any appreciable number of cases. It also seems likely that most of them are due to iron, although the likely contaminants copper, carbon, nickel and tungsten are probably the same in both cases. At any rate a majority of them do not seem to agree with strong inflections of these elements so far as they have been ascertained.

In view of the close similarity which is believed to exist between the atomic constitutions of iron (atomic number 26) and nickel (28) it is likely that they will have similar properties in the soft X-ray region. It therefore seems desirable to see if there is any evidence of a connection between the inflections found for nickel and those of iron. It seems likely that nickel will have a similar number of inflections to those for iron. The fact that we found a considerably smaller number is probably due to the absence of the improvements which we have since made with the apparatus. The nickel values are given in Table V in the first row. The second and third rows give the values for the next lower iron values found by us and by Thomas respectively. The fourth row gives the means of these values, where there are more than one, and the fifth gives the difference between the nickel value and the mean iron value. It will be seen that for every nickel discontinuity which we had already ruled on other grounds as likely to be authentic there is a corresponding iron discon-

tinuity. From 38.6 to 140.3 the difference only varies between 4.1 and 5.6, and there is evidence of a progressive increase in this difference in proceeding to higher voltages.

Table V.

Ni .....	38.6(3/0)	80.0(3/1)	88.9 (6)	99.0 (6)	140.3 (4)	245.5 (7)	281 (1)	288 (8)	316.4 (7) (335) (7)
Fe (R+C) .....		75.6 (2)	84.8 (2)	95.0 (3)	137.6 (6)	240.6(3/1)	270.2 (2)		
Fe (T) .....	34.3	75.3	82.7	94.8	131.8	228.1	277.4 (1.4)		303.7
Mean .....	34.3	75.5	83.8	94.9	134.7	234.4	273.8		303.7
Ni-Fe .....	4.3	4.5	5.1	4.1	5.6	11.1	8.2		12.7
Ni .....	392.4 (2)	433 (2)	532 (5)						
Fe (R+C) .....			498 (2)						
Fe (T) .....									
Mean .....			498						
Ni-Fe .....			34						

### § 6. Comparison of Total Radiations.

The data obtained in this investigation enable a preliminary estimate to be made of the relative efficiency of the four elements tested and also of their absolute efficiencies as emitters of X-rays in the range up to 600 equivalent volts. If the efficiency  $E$  is measured as the energy of the X-radiation emitted divided by the kinetic energy of the electrons impinging on the target, Beattie (21) has shown that his experimental results with ordinary X-rays are covered by the following approximate formula :—

$$E = 2.54 \times 10^{-4} B \left( \frac{v}{c} \right)^2, \quad (1)$$

where  $B$  is the atomic weight of the material of the target,  $v$  is the velocity of the impinging electrons, and  $c$  that of light. The calculations of Kramers (22) lead to the following equation for  $E$ , viz. :—

$$E = \frac{2\pi}{3\sqrt{3}} \frac{1}{l} \frac{e^2}{ch} N \left( \frac{v}{c} \right)^2 = 2.34 \times 10^{-4} N \left( \frac{v}{c} \right)^2. \quad (2)$$

Here

$$l = \log \frac{kv^3 m}{4\pi \bar{\nu}_t e^2}, \quad (3)$$

where  $k$  is a numerical constant = 1.1 which enters into Bohr's (23) theory of the stopping of rapidly moving electrified particles by matter,  $e$  and  $m$  are the electronic charge and mass,  $\bar{\nu}_t$  is the averaged frequency of revolution of the electrons in the stopping atoms,  $h$  is Planck's constant, and  $N$  the atomic number. The efficiency given by Kramers' formula is about half that found

by Beattie (since  $B \approx 2N$ ), but Kramers' calculations are for the general radiation only, whereas the experiments deal with the total radiation. There are also other differences; so that equation (1), which represents the experimental results, cannot be said to conflict with the theoretical equation (2). Another equation which is equivalent to (2) has been given by Kramers, viz. :—

$$I = \frac{\pi}{3\sqrt{3}} \times \frac{1}{l} \times \frac{e^2 m}{c^3 h} N v^4. \quad (4)$$

Here  $I$  is the average radiation energy which is emitted as a result of the impact of a single electron, velocity  $v$ , on the target.

It will be convenient so to deal with our results as to test if there is anything in the region of soft X-rays here investigated which corresponds with the foregoing relations.

The first step is to find the proportion of the total radiation emitted by the X-ray target which reaches the photoelectric testing chamber. The principle by which this is done may be illustrated by means of fig. 12, which represents

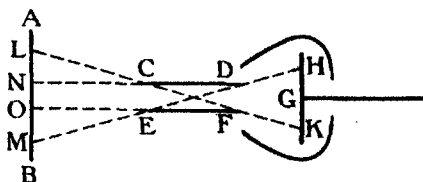


FIG. 12.

a simplification of the actual apparatus. Let  $AB$  represent the target  $CD$ ,  $EF$  the condenser plates, and  $G$  the photoelectric cathode. Let  $h = NO$  the width between the condenser plates,  $b =$  breadth of condenser plates,  $d =$  distance  $ND (= OF)$ ,  $x =$  distance  $NC (= OE)$ . Since the aperture is limited by  $DF$ , the average effective solid angle for the strip  $ON$  is  $hb/d^2$ , and for the strips  $LN$  and  $OM$  it is  $hb/2d^2$ , the angle  $LCN$  being regarded as small. The area of the strip  $ON$  is  $hb$ , and that of the strips  $LN + OM$  is  $2hb \frac{x}{d-x}$ .

We assume as a sufficient approximation to the truth that the electron current is confined to the front surface of the target and is spread uniformly over it. If this area is  $A$ , the proportion of the total emitted radiation which reaches the detecting plate  $G$  is thus

$$\frac{h^2 b^2}{4\pi A d^2} \left(1 + \frac{x}{d-x}\right) = \frac{h^2 b^2}{4\pi A d^2} \frac{d}{d-x}. \quad (5)$$

In the actual apparatus the angle LCN is not small, the target AB is inclined at an angle of about  $45^\circ$  to the line NCD, the radiation is limited also by the slit in the shielding cylinder in front of CE, which is not shown in fig. 17, and the condenser plates were not quite equal or parallel. For these reasons the formula (5) has not been used, but the corresponding factor has been evaluated graphically, using the same principles, from a sectional drawing of the actual apparatus. Its value is  $0.0455/4\pi$ . To obtain the photoelectric currents which would have been obtained if all the radiation generated by the target had been effective, the observed values must therefore be multiplied by  $4\pi/0.0455$ .

In our experiments the energy of the X-radiation is not measured directly, it can only be a matter of inference from the observed photoelectric currents. In the present computations we assume that

$$i_p = \alpha ne, \quad (6)$$

where  $i_p$  is the observed photoelectric current,  $\alpha$  is the number of electrons emitted per incident quantum of radiation, and  $n$  is the number of quanta of radiation incident on the target in unit time. The precise value of  $\alpha$  is a difficulty, but its value is not likely to vary much at the same primary voltage in all the experiments, since the photoelectric testing surface was of the same substance (copper) throughout. In general, the value of  $\alpha$  depends on the absorption of the radiation and of the photoelectrically emitted electrons in this surface, and on secondary emissions of electrons and radiations if they occur. For the special case in which there are no secondary emissions, and in which the X-radiation is completely absorbed and the photo-electrons not absorbed at all in the testing material, the value of  $\alpha$  is  $\frac{1}{2}$  (for the front surface only). In any event the uncertainty in  $\alpha$  can only affect seriously the absolute values and not the comparison of different X-ray target materials.

We have next to consider what is the average energy of a quantum of the radiation falling on the target. We know that when the primary voltage on the tube is  $V$  the maximum energy of a quantum is  $h\nu_{\max} = eV$ . We also know that this radiation contains all frequencies between  $\nu_{\max}$  and zero, and we assume, as a tentative working hypothesis, that the average value of the energy is approximately equal to  $\frac{1}{2}h\nu_{\max} = \frac{1}{2}eV$ . With these assumptions the energy of the X-radiation which gives rise to the measured photoelectric current  $i_p$  is

$$\frac{1}{2}neV = \frac{1}{2} \frac{i_p}{\alpha e} eV = \frac{i_p V}{2\alpha}, \quad (7)$$



and the energy of the X-radiation generated by the whole target when the potential on the tube is  $V$  is

$$\frac{2\pi}{0.0455\alpha} i_p V. \quad (8)$$

If the electronic current to the target is  $i_e$  the number per second of electron impacts generating the X-ray current is  $i_e/e$ , so that the energy liberated per electron impact on the target is

$$\frac{2\pi}{0.0455\alpha} \frac{i_p}{i_e} eV. \quad (9)$$

A set of values of  $i_p/i_e$  which have been recorded at or about 300 volts in the course of this investigation is shown in Table VI. When the actual voltages differ from 300 the values given in the third column for each element have been reduced to 300 volts by assuming that  $i_p/i_e$  is proportional to the applied voltage. This can be seen to be approximately correct by inspection of the preceding curves (figs. 4 to 11). The values for carbon are all in good agreement, except that the point taken on December 19, 1923, is rather high. This is probably due to all the gas not having been got out of the target at this stage. The reason for the three low values found for tungsten on March 10 and 27 and May 22, 1924, is not known. It may be that the slit in the shield had got moved from its usual position in these experiments, but as this is not sure they have been included in the table. The nickel values are all in good agreement among themselves. The two high values on October 18, 1924, are believed to be influenced by incomplete extraction of gas from the target, and the high values on November 21 and December 4, 1924, by deposition of tungsten on it. Only the first three iron values are comparable with the others, and the first two are believed to be influenced by incomplete gas extraction. The last 18 iron values were got by the direct deflection method and they depend on a knowledge of the magnitude of the xylol resistance. This is of the order  $10^{11}$  to  $10^{12}$  ohms, and, owing to the intervention of circumstances outside our control, we have not been able to measure it satisfactorily up to the present. These values also differ more than they should among themselves for some unknown reason. Taking the iron values as a whole, all that can be inferred from them at this stage is that the absolute value of the emission from this element is not very different from that for nickel.

It is clear from Table VI that the emission of soft X-rays under a given voltage increases much less rapidly with atomic number than it does in the ordinary

Table VI.

Carbon.			Tungsten.			Nickel.			Iron.		
Date of Observations.	Voltage.	At 300 V $\times 10^9$ .	Date of Observations.	Voltage.	At 300 V $\times 10^9$ .	Date of Observations.	Voltage.	At 300 V $\times 10^9$ .	Date of Observations.	Voltage.	At 300 V $\times 10^9$ .
19.12.23	303	1.985	5.3.24	300	7.36	18.9.24	303	4.27	14.1.25	288.6	4.60
17.1.24	300	1.44	10.3.24	305	4.97	"	297	4.33	15.1.25	289.2	4.37
18.1.24	300	1.45	27.3.24	300	3.89	9.10.24	300.9	3.49	19.1.25	300	3.64
6.2.24	300	1.48	13.5.24	303	8.10	"	297	3.47	18.3.25	300	4.62
7.2.24	300	1.51	13.5.24	297	7.65	22.10.24	303	3.83	"	300	4.45
			13.5.24	300	7.58	"	297	3.80	"	300	4.43
	Mean	1.57	22.5.24	300	4.14	24.10.24	300	3.48	21.5.25	306	5.12
			30.5.24	303	6.70	29.10.24	300	3.38	25.5.25	294	
			30.5.24	297	6.20	21.11.24	300	3.87	"	291	5.72
				Mean	6.29	4.12.24	300	4.25	12.6.25	300	4.90
									15.6.25	300	5.36
							Mean	3.82	18.6.25	300	5.37
									"	300	5.38
									24.6.25	300	4.20
									30.6.25	305	3.68
									"	295	3.69
									"	300	3.55
									1.7.25	304	5.26
									"	290	5.25
									2.7.25	292.5	3.85
									14.7.25	300	3.98
										Mean of last 18	4.70

X-ray region. In fact, instead of being proportional to the atomic weight or atomic number it is very nearly proportional to the square root of the latter, as may be seen from the last row of Table VII.

Table VII.

Element.	C.	W.	Ni.	Fe.
$i_p/i \times 10^9$ .....	1.57	6.29	3.82	(4.20)
Atomic No. N.....	6.0	74.0	28.0	26.0
$\sqrt{N}$ .....	2.45	8.6	5.29	5.1
$i_p/i \times 10^9$ .....	0.641	0.732	0.722	(0.824)
$i_p/i \times 10^9 / \sqrt{N}$ .....				

Apart from the different variation of the emission with atomic number there appears to be a close similarity between the efficiency of emission of these soft X-rays and those belonging to the more usually recognized X-ray region. The energy in both cases is approximately proportional to the square of the primary voltage, and the other factor entering into the absolute values is not very different in the two cases. The deviation from proportionality with the atomic number is perhaps not far to seek. According to the theory of Kramers this proportionality arises from the assumption that the electrons concerned in the generation of X-rays in the course of their motion through the target have sufficient velocity to enable them to penetrate through the outer shield of electrons into regions in the interior of the atoms where the field is governed mainly by the magnitude of the nuclear charge. It is not to be anticipated that the less energetic electrons dealt with in the present investigation will be able to do this. Assuming their penetrating power to be thus limited the fields encountered by the moving electrons will be more complicated and much feebler; but it may be permissible as a first approximation to assume that the phenomena are the same as if the nucleus were replaced by a nucleus of smaller charge  $N_e e$  where  $N_e$  is the effective atomic number. If we assume that Kramer's theory is capable of this modification the equation (4) becomes

$$I = \frac{4\pi}{3\sqrt{3}} \frac{1}{l} \frac{e^2 N_e}{c^3 m h} \times e^2 V^2 = 2\pi \left( \frac{2}{3\sqrt{3}} \frac{1}{l} \frac{e^3}{c^3 m h} \right) N_e V e V$$

$$= 2\pi \times 3.98 \times 10^{-8} N_e V. eV. \quad (10)$$

On the assumptions we have made this should be identical with (9), giving

$$N_e = 5.52 \times 10^8 \frac{i_p}{i_e} \times \frac{1}{V} \times \frac{1}{\alpha}. \quad (11)$$

In the present experiments  $\frac{i_p}{i_e} \times \frac{1}{V}$  was fairly constant for each target, and  $\alpha$  has the same value for the same radiation in all cases, since the same photo-electric testing plate was used. Thus,  $N_e$  does not vary much for a given substance over a moderate range of voltage: which is satisfactory. For  $1/V = 1$ , i.e.,  $V = 300$  volts, the data in Table VII give the following values of  $\alpha N_e$ :—for carbon 0.866, iron (2.32), nickel 2.11 and tungsten 3.47. It is fairly certain that  $\alpha$  is less than  $\frac{1}{2}$ ; if  $\alpha$  is equal to about  $\frac{1}{2}$  the resulting values of  $N_e$  are about equal in each case to the number of electrons per atom whose negative energies are generally considered to be smaller than or comparable with the energy of the electrons impinging on the primary target.

The apparatus used was not primarily adapted to determining with accuracy the data discussed in this section, but we believe that the accuracy, such as it is, is adequate for the deductions we have drawn from the data. It is intended to pursue further this phase of the investigation with different apparatus more particularly adapted to the purpose.

[*Note Added September 30, 1925.*— Since writing this paper we have noticed some observations by Holweck which have a close connection with the considerations put forward in this section.\* Holweck has measured the absorption in hydrogen, nitrogen and oxygen of heterogeneous soft X-rays generated under primary voltages over the range 123 to 300 volts. In 'C. Rendus,' 1921, p. 439, he gives the following values for  $\mu/\rho$  (the absorption coefficients reduced to unit density): for  $H_2$ ,  $\mu/\rho = 0.2\lambda^{5/2}$ , for  $N_2$ ,  $\mu/\rho = 0.8\lambda^{5/2}$ , and for  $O_2$ ,  $\mu/\rho = 1.0\lambda^{5/2}$ . Here  $\lambda$  is the equivalent average wave-length of the rays in  $10^{-8}$  cm., as deduced from the  $ch/\lambda = eV$  formula. These give the relative atomic absorption coefficients  $H = 0.2$ ,  $N = 11.2$ ,  $O = 16$ . For hard X-rays the atomic absorption coefficients vary as the 4th power of the atomic number.† If we assume that for soft X-rays these coefficients also vary as a power of the atomic number, and put, for example, the atomic absorption coefficient  $= CN^\alpha$ , where  $N$  is the atomic number and  $C$  and  $\alpha$  are constants, we find from the above data for  $H$  and  $N$   $\alpha = 2.10$ , and from the data for  $H$  and  $O$   $\alpha = 2.11$ . In a later paper Holweck‡ gives the figures  $\mu/\rho$  for  $N_2 = 0.7\lambda^{5/2}$ , and for  $O_2$   $\mu/\rho = 0.9\lambda^{5/2}$ . These treated in the same way give  $\alpha = 1.8$  and  $2.06$  respectively. It thus appears that the atomic absorption coefficients for soft X-rays vary as the square of the atomic number, instead of the 4th power, at any rate approximately. This result and the data about excitation efficiency given in the present paper furnish us with the following interesting table:—

	For Hard X-rays.	For Soft X-rays.
Excitation efficiency proportional to .....	$N$	$N^{\frac{1}{2}}$ approx.
Atomic absorption coefficient proportional to .....	$N^4$	$N^2$ approx.

If we call the factor by which the atomic number enters into the expression for the excitation efficiency  $x$  it appears that in each class of X-rays the atomic

\* There is an element of uncertainty in this, as we do not know what allowance should be made for scattering of the radiation. But inasmuch as, even for hydrogen, Holweck's absorption coefficients vary as  $\lambda^{5/2}$ , there would appear to be a strong presumption that the greater part of his measured absorption was not caused by scattering.

† Bragg and Pierce, 'Phil. Mag.,' vol. 28, p. 626 (1914); H. Moore, *ibid.*, vol. 27, p. 177 (1914); 'Roy. Soc. Proc.,' A, vol. 91, p. 337 (1915).

‡ 'Ann. de Chim. et de Phys.,' vol. 17, p. 40 (1922).

absorption coefficient varies as  $x^4$ . This can be harmonised with the type of argument used by Kramers\* if we assume that the electron encounters, which are effective in the production of the hard X-rays, occur in the strong fields near the nuclei, whereas for the soft X-rays the electron encounters are confined to the weak fields nearer the outside of the atom. While this distinction is undoubtedly valid and important, it would be premature to assume at this stage that it furnishes a complete explanation of the phenomena. Another way of summarising the information in this table is to say that the soft X-ray phenomena are dominated by a reduced effective atomic number  $N_e$ , which is proportional to the square root of the actual atomic number  $N$ ; then just as for hard X-rays the excitation efficiency and atomic absorption coefficients are proportional respectively to  $N$  and  $N^4$ , so for soft X-rays the corresponding quantities are proportional to  $N_e$  and  $N_e^4$ .]

#### § 7. General.

In the preceding section no attempt has been made to separate effects due to characteristic X-radiations from those due to general X-radiation. Far too little is known about the phenomena to enable this to be done at present. Some writers (24), following Foote and Möhler (25) and K. T. Compton (26), have interpreted inflections with the subsequent rise concave upwards or straight as the equivalent of ionisation potentials, and those with the rise concave downwards as radiating potentials. It seems very doubtful whether this criterion is of any value. Some of the inflections observed in the present investigation are followed by curves which may for the same inflection be either convex upward, straight, or convex downward, depending in some obscure way on the conditions. Moreover, some observations which it is hoped to publish shortly obtained by one of us (O. W. R.) and Prof. Tanaka on the phenomena at the radiating and ionising potentials of helium show a like variability. It may be that under some carefully-controlled conditions which might be capable of specification in the case of gas ionisation such a distinction might be valid, but it would seem at the present stage a very unsafe guide in the case of soft X-ray phenomena.

Discontinuities in primary X-ray emission may arise from any of the following phenomena :

(1) Analogous to ionisation potentials. An electron is displaced by the impact at a critical potential from an internal energy level to a point outside the atom and subsequently returns with emission of characteristic radiation.

(2) The same phenomenon except that the electron does not get entirely

\* *Loc. cit.*

free of the atom, but moves to an outlying orbit from which it subsequently returns with emission of radiation. This is analogous to a radiation potential.

(3) This is the same case as the last, except that the second orbit is metastable. In this case there is no emission of characteristic radiation.

These three sources of discontinuities have long been recognized. It is believed that the two following are new, at any rate in this connection.

(4) The existence of possible orbits within the atom which are not normally occupied admits of phenomena analogous to those under (2) and (3) without the displaced electron leaving the atom, and of the existence of internally excited atoms. There is evidence in support of phenomena of this kind in the ordinary X-ray field.

(5) If the considerations towards the end of § 6 are sound it is likely that some of the discontinuities will have no connection with the excitation of secondary rays or with the phenomena associated with metastable states, but will be properties of the general radiation from the atom. In fact if we can treat the structure of the atom as analogous to that of a nucleus surrounded by a series of shells, there will be a series of critical potentials at which the impinging electrons are enabled to penetrate each set of shells in succession, and depending on whether the new accession of electric field is weaker or stronger, the rate of increase of emission of X-rays will diminish or increase. Thus the investigation of these discontinuities may be a way of investigating the internal structure of the atom as it exists as a whole apart from the possible displacements of individual electrons from their normal orbits.

It is felt that the possibilities just enumerated should be sufficient to account for the large number of discontinuities which have been observed, but it would appear to be premature at present to make further attempts to allocate specific causes to individual discontinuities.

#### § 8. *Summary.*

(1) In this paper a photoelectric method and apparatus are described for investigating the excitation of soft X-rays.

(2) The phenomena between about 40 and 600 volts are described in detail for carbon, nickel, iron and tungsten.

(3) When the curves between efficiency of X-ray emission and primary voltage are plotted a number of abrupt changes of slope are observed. Within the range 40–600 volts four such discontinuities, of which the lowest one is complex, have been observed for carbon, 13 for tungsten, 10 to 13 for nickel, and 15 for iron.

(4) Some of these discontinuities are due to the excitation of characteristic

X-rays and allied phenomena. Others are probably due to discontinuities in the general X-radiation which arise from the discontinuousness of the electronic structure of atoms.

(5) The total X-radiation per electron impact is approximately proportional to the square root of the atomic number for the target elements tested, and to the square of the energy of the impinging electrons.

(6) If we suppose the effective atomic number of the emitting target element to be appropriately reduced the remaining factor which determines the absolute emission is not very different from that operative in the ordinary X-ray region of higher frequency.

§ 9. In conclusion we wish to acknowledge our indebtedness to the Department of Scientific and Industrial Research, and to the Education Committee of the Kent County Council, for pecuniary assistance to one of us (F.C.C.) which has enabled this research to be brought to the present stage.

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- (24) e.g. Thomas (*loc. cit.*).
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*Immobile Groups of Atoms with Strong Specific External Fields  
as the cause of Catalytic Activity.*

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In the case of chemical reactions which occur in adsorbed films, without the formation of definite intermediate compounds, much evidence has been given showing that the catalyst surface is not uniformly active, and that chemical reaction only occurs on particular centres which occupy a small fraction of the whole surface. Taylor\* has recently developed a theory of the catalytic surface in which the activity is attributed to atoms whose fields are highly unsaturated, and which therefore constitute the centres of activity.† In view of the fundamental importance of a precise knowledge of the nature of these active centres in any general theory of catalysis, and the fact that electrolytically‡ deposited copper is inactive towards alcoholic substances at temperatures at which reduced copper causes rapid reaction, a study was made of the methods of preparing catalytically active copper in the hope of obtaining useful information concerning the structure of the centres themselves.

Considerations of probability show that as a first approximation the number of centres present with a given heat of activation is an exponential function of the heat of activation on each.§ Such a surface causes chemical reaction, as if it were composed of centres having the least value of the heat of activation in the exponential distribution. Thus the temperature coefficient of chemical change in heterogeneous catalysis is normally determined by the most active centres on the surface.

Pure metallic copper was made in many ways, and the heat of activation on the most active centres measured as shown in the catalytic decomposition of pure dry ethyl alcohol into acetaldehyde and hydrogen. The relative surface activities of the preparations were also compared. The technique of these determinations was well known and has been previously described.||

\* 'Roy. Soc. Proc.,' A, vol. 108, p. 105 (1925).

† Constable, *ibid.*, A, vol. 107, p. 274 (1925).

‡ Palmer, *ibid.*, A, vol. 98, p. 16 (1920).

§ Constable, *ibid.*, A, vol. 108, p. 374 (1925).

|| Palmer and Constable, *ibid.*, A, vol. 106, p. 251, vol. 107, p. 255. Constable, 'Proc. Camb. Phil. Soc.,' vol. 22, No. 5, p. 738 (1925).



Some further modifications were made in the details of the apparatus, the receiver J ('Roy. Soc. Proc.,' A, vol. 106, p. 252, fig. 1) being made to maintain a constant level of liquid, and the reaction tube being modified to diminish temperature lag between the heating and cooling experiments.

#### EXPERIMENTAL.

##### *Methods of Preparation giving Inactive Copper.*

(1) The copper was deposited electrolytically from a solution of pure twice-recrystallized copper sulphate on cleaned copper gauze with a current density of 0.01 amperes per square centimetre. The gauze was then made into spirals 10 cms. long, each having a surface area of 200 sq. cms., and being of such diameter that they would fit a glass combustion tube easily.

Eight of these spirals were tested together and were found to be inactive at all temperatures tried up to 370° C.

(2) Copper was deposited from ammoniacal solution, using hydrazine hydrate as reducing agent, on both copper gauze and glass tube cut into small pieces.

Three grams of copper acetate were dissolved in 100 c.c. water, and ammonia added till the precipitate formed just dissolved. Hydrazine hydrate was added drop by drop till the solution became colourless; the object to be coated was placed in the solution and heated by a hot-water bath. Excellent copper mirrors were obtained.

These preparations were also inactive at temperatures up to 370° C.

(3) Commercial copper gauze was rubbed with a steel file till bright and metallic. The gauze was then rolled up as before and ten rolls tested. No activity was found.

(4) The gauze was hammered with a clean steel hammer on a steel anvil. No change in activity was produced.

(5) Ordinary commercial copper gauze, washed with absolute alcohol, was used. It was also found inactive.

(6) Copper foil was polished with rouge. No activity was found.

##### *Method of Testing for Traces of Activity.*

Eight spirals were packed into the tube of a combustion furnace, and carbon dioxide passed through till the tube had warmed up to 100° C. Absolute alcohol contained in a 300 c.c. distilling flask was then electrically boiled over the copper, the issuing vapour being condensed, and the end of the condenser dipping under the liquid so that any slight evolution of gas could be detected.

In the case of all six preparations the tube was slowly heated up to about 370° C., no evolution of gas being detected.

The liquid distillate was fractionated through a Dufton column, and the first fractions tested for aldehyde by means of *p*-nitro-phenyl hydrazine. Only in the case of commercial copper gauze was the slightest trace of hydrazone obtained. This test for activity is even more delicate than the absence of evolution of gas, since the whole of the reaction products are contained in the first fraction of the distillate. Thus none of the preparations gave evidence of activity.

*Quantitative Comparison of the Surface Activity of these Preparations with Copper reduced below 300° C.*

Let  $a$  = the radius of the wire of the gauze,

$l$  = the length and breadth of the piece of gauze wound into the spiral,

$n$  = the number of strands per unit length,

then area of one wire of length  $l$  and radius  $a$  =  $2\pi al$ .

The number of wires in the piece =  $2nl$ , hence the total surface area =  $4\pi anl^2$ . The area of eight spirals when  $a = 0.0155$ ,  $n = 14$ ,  $l = 10$ , becomes 2000 sq. cms.

To obtain the area of the copper films used as catalysts it is sufficient to know the mass of copper used, and the mean grain diameter. The mass of copper used varied only slightly from 0.01 gm. From the size of the copper atoms it is evident that the grain diameter cannot fall much below  $10^{-7}$  cms. If

$r$  = the mean grain diameter,

$\rho$  = the density of grains, of which there are  $n$ ,

$S$  = the total surface area of the catalyst,

$m$  = the total mass,

then

$$m = \frac{4}{3} \rho \pi n r^3, \text{ and } S = 4\pi nr^2.$$

Hence  $S = 3m/\rho r$ , and the maximum possible area becomes 33,000 sq. cms. Hinshelwood's values for the grain diameter vary from  $10^{-8}$  to  $10^{-6}$  cms.\* and values of  $S$  from 3.3 to 330 sq. cms. The area of the plane film calculated from the dimensions of the rods amounts to 32 sq. cms. The probable value of the grain diameter thus becomes of the order of  $10^{-6}$  cms.

\* 'Roy. Soc. Proc.,' A, vol. 102, p. 318.

It now remains to calculate the ratio of the reaction velocity at 370° and 200° C., from the known value of the heat of activation.

If

$v_2$  = the rate of reaction at  $T_2$ , and  $v_1$  at  $T_1$  Å,

then

$$v_2 = Ae^{-\epsilon/RT_2} \quad \text{and} \quad v_1 = Ae^{-\epsilon/RT_1}$$

or

$$v_2/v_1 = e^{-\epsilon/R \left( \frac{1}{T_2} - \frac{1}{T_1} \right)}.$$

Hence

$$\log_{10} \frac{v_2}{v_1} = \frac{0.434\epsilon}{R} \left\{ \frac{1}{T_1} - \frac{1}{T_2} \right\}.$$

But

$$\epsilon = 20,000 \text{ cal.}, \quad T_1 = 473 \text{ Å}, \quad T_2 = 643 \text{ Å},$$

therefore

$$v_2/v_1 = 270.$$

The ratio of the surface exposed by the inactive copper is at least 1/16th, but more probably 18 times that of the reduced copper. Thus, the rate of reaction per unit area on the inactive copper is at most 1/20th, and is probably less than 1/5000th that occurring on other preparations of active copper, and we have clear evidence that the mere surface exposed by the preparations is insufficient to explain the divergence in catalytic effects.

#### *Methods of Preparation giving Active Copper.*

(1) *Rapid Condensation of Copper Vapour.*—The china-clay rods used in previous experiments were wrapped round with fine copper wire, and a heavy current from accumulators passed through the wire. The volatilised metal was very rapidly cooled by the objects on which it condensed. The first experiments that were tried failed to produce an active copper, but it was found that the reddish-yellow deposit was completely soluble in cold hydrochloric acid, and was therefore cuprous oxide. The nitrogen gas in which the volatilisation occurred was very carefully freed from oxygen by passing repeatedly over red-hot copper, and the wire was volatilised in the tube in which the reaction with alcohol was to occur. When these precautions were taken, it was found that the metal possessed a considerable activity.

Attempts were made to deposit copper by means of the electric arc between copper wires, but these met with failure, chiefly owing to failure to prevent oxidation.

The measurements obtained are shown in Curve VI, fig. 1. It is to be observed that the temperature coefficient of the chemical change is very little

different to that obtained with reduced copper ( $\epsilon = 19,400$  cals. per gram mol.).

(2) *Violent Agitation of Copper Atoms in the Metallic Surface at High Temperature.*—When a slow current of ammonia is passed over copper gauze at  $820^{\circ}$  C. the gauze loses its metallic lustre and becomes pink in colour, the individual wires of the structure retaining their form, though becoming very brittle and pitted in appearance. At the same time the ammonia is decomposed into its elements.\* The copper is unchanged in composition with slow rates of passage of gas. After five hours at  $820^{\circ}$  C. the weight of a piece of gauze altered from 14.03 to 14.02 grams, hence there is no appreciable formation of nitride under these conditions, and the copper is pure. Beilby and Henderson (*loc. cit.*) state, "this alteration in the metal seems to point to the formation and subsequent decomposition of a nitride which is only stable within a short range of temperature. Observation with the microscope showed that the copper had become spongy and disintegrated throughout. It retained its colour and, to a certain extent, its metallic lustre, but appeared as though it had been in the fluid state and blown up into a sponge by innumerable gas bubbles." These observations were confirmed. The surface was also found to be pitted. After use as a catalyst at temperatures from  $220^{\circ}$  to  $270^{\circ}$  C. for about two to three hours it was observed that the metallic appearance was almost completely regained, but that there was very little alteration in the catalytic activity. Microscopic examination showed that the surface had become much more regular, due to the smoothing-out of the larger pits, the very small pits being still very obvious. The difference between this active surface and the clear-cut surface of inactive copper shows that the presence of catalytic activity is to be connected with the small pits in the surface and the consequent irregular arrangement of the surface atoms. The larger irregularities have no effect on the catalysis.

Copper prepared in this manner is moderately active, the activity being practically independent of the subsequent treatment after heating in ammonia, little difference being found in the activity of copper allowed to cool slowly in ammonia and metal quenched from  $820^{\circ}$  C. in cold water. Considerable increase in activity was caused by alternate oxidation and reduction by ammonia and air at these elevated temperatures, a maximum activity being reached which was, however, much less than that obtained by reduction with carbon monoxide at  $300^{\circ}$  C. (see Table I, col. 9). These data are shown graphically in fig. 1. The catalyst could also be exposed to air

\* Beilby and Henderson, 'J. Chem. Soc.,' vol. 79, p. 1245 (1901).

for several hours without loss of activity, though after a day some traces of cuprous oxide could be seen on the surface, especially where steel shears had been used to cut the active product into strips.

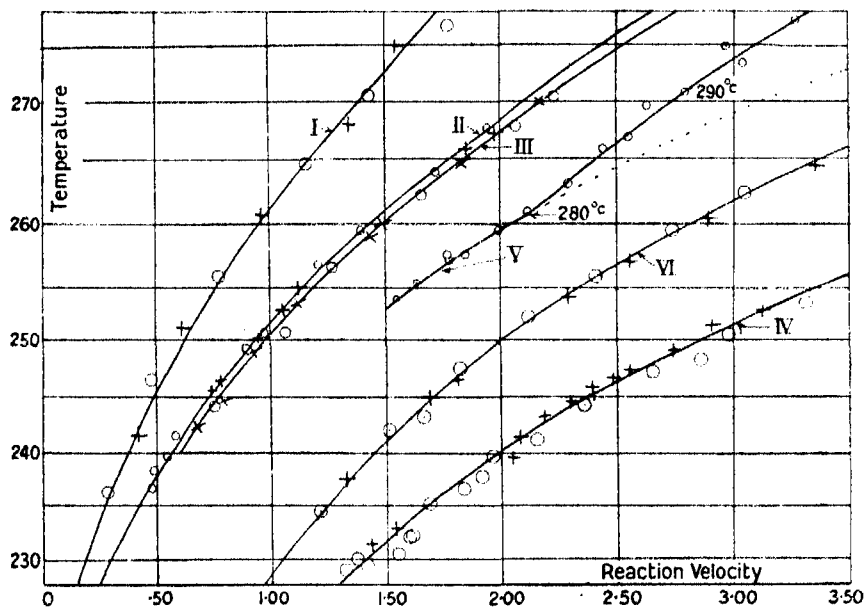


FIG. 1.—Activation by rapid condensation and catalytic action.

Curve I represents the reaction velocity temperature curves for copper after being heated\* to 820° C. for two hours with ammonia and transferred through air to the reaction tube. Curves II and III were not obtained by cooling the copper from 820° C. in ammonia, as before. The gauze was quenched in cold water from redness. The silica tube, with the current of ammonia still running, was placed with its end under water and tapped till the red-hot copper fell into the water. Two experiments gave agreeing results, and also owing to the good thermal conductivity of the metallic catalyst rapid heating and cooling curves would overlap. The temperature coefficient is distinctly higher than that of activated reduced copper.

Curve IV shows that the activity of the catalyst is increased by alternate oxidation and reduction with ammonia and air, and the results (Table I) show that the temperature coefficient is also diminished. The temperature at which the copper surface commences to be poisoned by the polymerisation

\* I am much indebted to Mr. C. T. Heycock, F.R.S., for the loan of an optical pyrometer by means of which the temperature was measured

of the aldehyde is unchanged by this method of activation (Curve V). Thus though the temperature at which polymerisation commences to occur is unaltered, there is some alteration in the temperature coefficient of chemical reaction. The numerical results obtained, together with the calculated heat of activation and the values of the reaction velocity calculated therefrom, are shown in Table I.

Table I.—Electrolytic Copper activated by Ammonia at 820° C.

Number of curve (Fig. 1):---	I.		II.		III.	IV.		Col. 9.
Temperature ° C	Reaction velocity c.c.s. H <sub>2</sub> per min.							
	Obs.	Calc.	Obs.	Calc.	Obs.	Obs.	Calc.	Obs.
225 .....	—	—	—	—	—	1.12	1.12	—
230 .....	0.20	0.22	—	—	—	1.37	1.38	—
235 .....	0.27	0.28	0.44	0.45	0.44	1.69	1.66	—
240 .....	0.37	0.36	0.57	0.57	0.59	2.02	2.01	—
245 .....	0.48	0.46	0.73	0.72	0.77	2.38	2.40	—
250 .....	0.60	0.59	0.94	0.93	0.98	2.91	2.90	—
255 .....	0.73	0.74	1.14	1.15	1.19	3.50	3.47	—
260 .....	0.94	0.93	1.44	1.44	1.50	—	—	—
265 .....	1.15	1.17	1.78	1.76	1.84	—	—	—
270 .....	1.37	1.48	2.16	2.18	2.18	—	—	47.0
<hr/>								
Intercept on logarithmic curve ....	1.13		1.10		0.87			
<hr/>								
Heat of activation ....	25,600		25,200		19,800 cals. per gram molecule.			

### (3) Production of Metallic Copper by Rapid Chemical Reaction.

(a) *Reduction of Cupric and Cuprous Oxides by Carbon Monoxide.*—Considerable interest attaches to the comparison of the catalytic activity of copper reduced from these two oxides, since the theory put forward by Palmer to explain the inactivity of electrolytic copper, the effect of temperature of reduction on the activity, and the effect of various reducing agents,\* states that the two oxides will give copper of different activity.

The oxides were supported on china-clay rods, as in previous experiments. Trial showed that if the rods were roughened, damped with distilled water and rolled in the finely divided cuprous† or cupric oxide,‡ an adhering film was formed, and by experience gained in making a considerable number of

\* Palmer, 'Roy. Soc. Proc.,' A, vol. 98, p. 23 (1920), vol. 99, p. 420 (1921).

† Prepared from Fehling's solution and glucose, and well washed with water.

‡ For prep. see 'Roy. Soc. Proc.,' A, vol. 106, p. 251 (1924).

these rods, it was possible to get the same weight of copper on each rod with an accuracy of about 5 per cent. The technique of the further comparison of activity was as before, except that a reduction temperature of 320° C. was used and the films were activated by alternate oxidation and reduction. The observations are shown in Table II, and give no evidence in support of Palmer's

Table II.—The Comparison of the Activity of Equal Masses of Copper from Cuprous and Cupric Oxides.\*

Temperature, ° C.	Reaction velocity.		
No. of alternate oxidations and reductions.	Cuprous oxide.		
	0.	1.	2.
225.....	0.110	0.165	0.176
230.....	0.130	0.209	0.231
235.....	0.168	0.252	0.277
240.....	0.205	0.307	0.340
245.....	0.250	0.375	0.410
250.....	0.323	0.484	0.535

Heat of activation deduced, 22,300 cal. per gram molecule.

No. of alternate oxidations and reductions.	Cupric oxide.		
	0.	1.	2.
225.....	0.104	0.155	0.165
230.....	0.132	0.198	0.221
235.....	0.160	0.239	0.263
240.....	0.195	0.282	0.317
245.....	0.246	0.355	0.391
250.....	0.307	0.464	0.511

Heat of activation deduced, 22,500 cal. per gram molecule.

\* For a study of activation carried further, see Constable, 'Roy. Soc. Proc.,' A, vol. 107 (1925).

theory. The activity of copper produced from cuprous and cupric oxides is very nearly the same, and on activation both films behave in the same manner. The grain-size of the two oxides may have some effect on this comparison, but in view of the similarity of the increase in activity on activation of copper from both these oxides and copper from the copper salts of the fatty acids, this effect is probably small.

(b) *The Thermal Decomposition of the Copper Salts of the Monobasic Fatty Acids.*—The copper salts were made from copper carbonate, prepared from pure electrolytic copper, and the redistilled fatty acids. Formate and acetate were crystallized from water containing excess of the acid. Propionate and butyrate were extracted from aqueous solution with chloroform and repeatedly recrystallized to free from excess of fatty acid. Both salts were finally once crystallized

from alcohol. Copper valerate was precipitated from an aqueous solution of the acetate by valeric acid and purified by crystallization from benzene.

The temperature at which these copper salts decomposed into metallic copper was determined both by heating in a glass tube through which a current of carbon dioxide was passing, and by observing the temperature at which the salts became catalytically active when heated in a stream of alcohol vapour (fig. 2). Nichrome wire was uniformly wound round a glass tube leaving an interval of about 0.5 cm. between each wire. In this way a uniform temperature could be obtained along the tube. Control of temperature was secured by regulating the heating current, and at the same time the decomposition of the copper salt, contained in a small boat, could be observed through the wires. A mercury thermometer beside the boat measured the temperature of the enclosure, and thus the temperature of decomposition.

Table III.—The Thermal Decomposition of Copper Salts.

Salt.	Temperature, ° C.	Nature of products.
Formate .....	100	Gives off water of crystallization, and becomes deeper blue.
	180	Slight darkening.
	190	Darkening marked, and decrepitation of individual crystals.
	200	Metallic copper observed.
	210	Decomposition complete.
Acetate .....	150	Darkens.
	245	Gives off acetic acid in considerable quantity.
	260	Traces of copper noticed; if temperature be maintained, copper is deposited on the glass containing tube.
	270	Decomposition complete.
Propionate .....	275	Decomposition complete.
Valerate .....	285	Decomposition complete.
Oxalate .....	300	Darkens.
	305	Brown copper visible.
	315	Complete.
Malonate* .....	280	Darkens.
	300	Copper visible.
	310	Complete.
Succinate* .....	270	Tinge of brown.
	330	General darkening.
	340	Fumes.
	345	Rapid change to copper colour.
	355	Copper throughout.

\* I am indebted to Mr. L. V. Wright, M.A., F.I.C., of Northampton School, for these results.



Investigation showed that with the copper salts of the fatty acids, some fatty acid was liberated and metallic copper left. Formate gave pure copper in quantitative yield. The higher fatty acids also gave a quantitative yield (Table IV) of metal, but in these cases it was contaminated with traces of organic matter, which caused discolouration when the copper was dissolved in nitric acid.

In view of the poisonous nature of free fatty acids on catalytic activity it is not surprising that the copper salts when heated in still nitrogen gas leave copper which is only slightly active. Fig. 3, Curve I shows copper formate, Curve II acetate, under these conditions. When a rapid stream of alcohol vapour was used to remove the fatty acid, Curves IIIc and h and IVc and h were obtained for the cooling and heating curves respectively, and a very considerable activity is found. A fast stream of nitrogen gas was also effective in producing a highly active product. In both cases the red-brown colour of the product was in marked contrast to the metallic nature of the copper obtained by reduction from oxide.

The former method of obtaining the salt on the supporting rods by impregnation under reduced pressure by a saturated solution\* was abandoned in favour of a quicker method. A warm saturated aqueous solution of the

Table IV.

Copper Salt.	Formula.	Calculated percentage of copper.	Percentage weight left when heated in a rose crucible in carbon dioxide.
Formate* .....	$\left\{ \begin{smallmatrix} \text{H.CO.O} \\ \text{H.CO.O} \end{smallmatrix} \right\} \text{Cu.4H}_2\text{O}$ .....	28.3	28.6 28.4
Acetate .....	$\left\{ \begin{smallmatrix} \text{CH}_3\text{CO.O} \\ \text{CH}_3\text{CO.O} \end{smallmatrix} \right\} \text{Cu.H}_2\text{O}$ .....	31.8	31.9 32.0
Propionate .....	$\left\{ \begin{smallmatrix} \text{C}_2\text{H}_5\text{CO.O} \\ \text{C}_2\text{H}_5\text{CO.O} \end{smallmatrix} \right\} \text{Cu.H}_2\text{O}$ .....	27.9	28.2 28.1
Oxalate .....	$\left\{ \begin{smallmatrix} \text{CO.O} \\ \text{CO.O} \end{smallmatrix} \right\} \text{Cu}$ .....	42.0	42.9 42.5

\* There are many hydrates of this salt; measurement of the water given off on heating confirmed that the tetrahydrate was the one used.

formate or acetate was drawn up into a glass tube with a narrowed end. On rubbing the drawn-out end of the tube on the supporting rods the salt formed

\* Palmer, 'Roy. Soc. Proc.,' A, vol. 98, p. 20 (1920).

a fine layer of crystals over the surface. By rubbing this layer with a glass rod till the coating was of uniform colour very uniform surface deposits could be obtained.

With propionate, butyrate and valerate the simpler method of wetting the rods with a saturated solution of the salt in absolute alcohol, and allowing the alcohol to evaporate off gave excellent results. A thin, tenacious coating of the salt resembling coloured celluloid was obtained. Careful handling is however necessary, as the coating flakes off if sharply tapped. The amount of copper used on six rods was of the order of 0.01 to 0.02 gram. The precise magnitude of the quantity used is unimportant, as the method of comparing the surface activities depending on the behaviour of the films on activation renders a knowledge of the mass of copper used unnecessary.

The rods were placed in the nitrogen-filled reaction tube, which was warmed to 100° C.; the stream of alcohol vapour was then turned on and the reaction tube rapidly heated to about 260°. The subsequent heating to 280° (about) was much lower. Measurements of time, temperature and reaction velocity were made in this last temperature interval, in which the salts decomposed into metallic copper. The data obtained are shown in fig. 2, and confirm the visual observations.

The catalyst obtained is quite stable, and the activity attained after six minutes persists for hours. The overlapping of heating and cooling measurements also confirms this evidence of stability. Sometimes the catalyst showed a slowly falling activity, but this was not often met with. It is suggested that in these cases complete removal of the fatty acid from the reaction tube had not occurred, and the subsequent adsorption by the copper poisoned the catalyst. The measurements of the reaction velocity obtained on cooling and reheating are given separately (fig. 3, Curves III and IV). Since the surface is gradually being covered up the cooling curve shows too great, the heating curve too small, a temperature coefficient, the mean value lying near the true value. From such measurements it is easy to see the magnitude of the error caused by deducing the temperature coefficient from the heating or cooling curve alone (about 10 per cent.).

When overlapping occurred the reaction velocity temperature curves were drawn, and in addition the catalyst was activated by alternate oxidation and reduction at 300° C., two additional curves being given in each case (Table V). It was found in the case of copper from the salts of the monobasic fatty acids that the maximum activity was practically reached at the first oxidation and reduction, the activity after the next oxidation and reduction being only

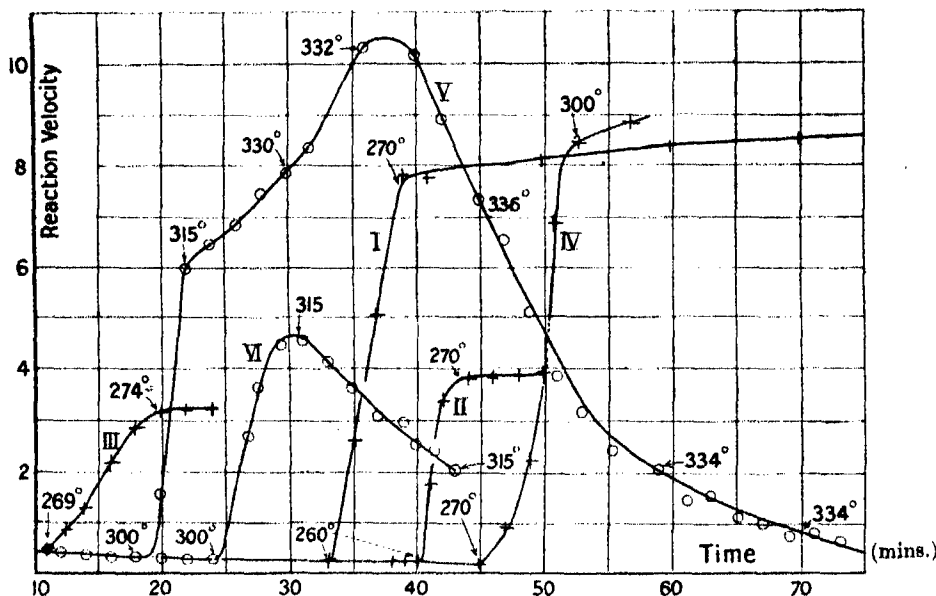


FIG. 2.—The Birth of Activity by Thermal Decomposition.

Curves I and II	...	...	Copper acetate.
Curve III	...	...	.. propionate.
Curve IV	...	...	.. valerate.
Curves V and VI	...	...	.. oxalate.

The flag labels give the temperatures at the points indicated. The straight line from which the curves commence represents the nitrogen evolution from the reaction tube and does not show that the undecomposed salt possesses an activity of its own. The final values of the activity at constant temperature shown in Curves I, II and III could be maintained for many hours.

very slightly greater. Since the limiting value of the catalytic activity depends only on the mass of copper used as catalyst and not on its origin, the comparison of the initial activity with the limiting activity on activation gives a measure of the surface activity of the original preparation. Such a comparison is more advantageous than a comparison per unit mass of copper, since all errors due to varying conditions of experiment with various preparations are eliminated. The results obtained are shown in figs. 3 and 4.

It can be seen that the temperature coefficients of chemical action on the various preparations do not vary widely, and the surface activity is nearly the same in all cases, in spite of the fact that the distribution of the copper atoms in the original salts varied very widely.

(c) *The Thermal Decomposition of the Copper Salts of the Di-basic Acids.*—The salts were prepared by precipitation. The acid was nearly neutralised by a

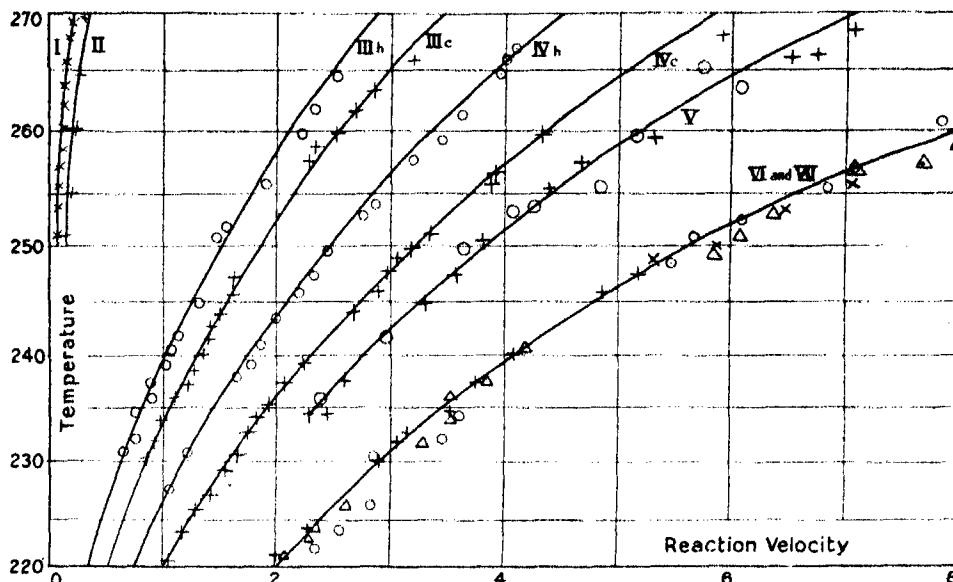


FIG. 3.—Copper from acetate and formate. Curves I and II show feebly active preparations of copper from the decomposition of the salts of the acids in still nitrogen gas. Active preparations were made by rapidly removing the reaction products in a stream of alcohol vapour. Curves III<sub>h</sub> and *c* and IV<sub>h</sub> and *c* show copper from acetate giving an unstable catalyst. Curves V, VI and VII show the increase in the activity of a catalyst (V) on alternate oxidation and reduction at temperatures below 300° C.

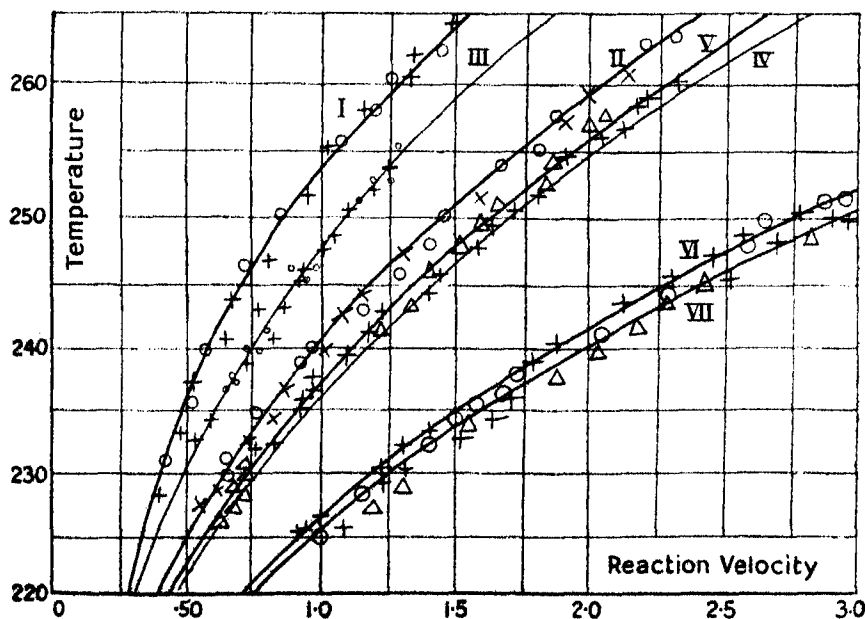


FIG. 4.—Copper from formate, propionate and valerate. Copper catalysts produced by thermal decomposition, and activated by alternate oxidation and reduction below 300° C. Curves I and II show copper from formate. Curves III and IV show copper from propionate. Curves V, VI, and VII show copper from valerate. (See Table V.)

Table V.—A Typical Catalyst from Copper Valerate (fig. IV, Curves V, VI and VII), with a summary of the Results with other Preparations of Copper.  
(No. of oxidations and reductions.)

Temperature.	0		1		2		Ratios.	
	Reaction velocity.							
	$v_0$		$v_1$		$v_2$		$v_0/v_1$	$v_0/v_2$
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.		
225 .....	—	—	0.94	1.00	1.00	1.07	—	—
230 .....	0.72	0.74	1.23	1.26	1.32	1.32	0.57	0.54
235 .....	0.90	0.90	1.57	1.51	1.65	1.65	0.57	0.54
240 .....	1.12	1.09	1.93	1.86	2.02	2.03	0.59	0.54
245 .....	1.37	1.32	2.34	2.34	2.47	2.46	0.59	0.54
250 .....	1.63	1.65	2.84	2.85	3.01	2.97	0.57	0.54
255 .....	1.94	1.93	3.48	3.55	3.68	3.67	0.55	0.53
260 .....	2.32	2.29	—	—	—	—	—	—
265 .....	2.71	2.67	—	—	—	—	—	—
Relative initial activity .....							0.57	0.54
Mean .....							0.56	
Intercept on logarithmic curve—			0.95		0.94		—	
Heat of activation—			21,600		21,400		—	

Relative Surface Activities of Copper Preparations.	Heat of Activation.
From—	cal. per gm. mol.
Formate = 0.61	19,800
Acetate = 0.67	19,700
Propionate = 0.62	19,800
Valerate = 0.56	20,070
Cuprous	
oxide = 0.63	22,300
Cupric	
oxide = 0.63	22,500

solution of ammonium carbonate\* and the filtrate precipitated by a solution of copper sulphate. The insoluble salt was purified by washing.

The damped supporting rods were rolled in the dry salt and placed, covered with the adhering layer, in the reaction tube. Since decomposition into metallic copper only occurs above 280° C. (see Table III), a maximum activity occurs, followed by a rapid decay, when the birth of the activity is observed. Such observations are shown in fig. 2. When the reaction tube is rapidly cooled after the production of the copper the product retains sufficient activity for accurate temperature coefficient measurement to be made. The value obtained

\* Gantter and Hell, 'Ber.,' vol. 17, pp. 2, 216 (1884).

was normal for oxalate and malonate, but with succinate the measurements could not be made.

The copper is obtained in the form of a dull brown powder.

(d) *The Thermal Decomposition of the Copper Salts of Tartaric and Citric Acids.*—Both salts decompose at a relatively low temperature, and give active copper. The metal is, however, mixed with a considerable amount of carbon. Experiment showed that the carbon had no effect on the temperature coefficient of reaction at the surface.

*The Effect of the Method of Preparation of Copper on the Temperature at which Poisoning by the Reaction Products becomes Evident.*

The shape of the curves obtained for the temperature ranges including  $280^{\circ}\text{C}$ . and above are markedly influenced by the rate of heating. With slow rates a very pronounced cusp can be obtained. With very fast rates the activity very gradually falls below the value calculated from the exponential law. The five curves in fig. 5 obtained for preparations of copper by volatilisation (I), and by thermal decomposition of copper formate (IV), acetate (II), propionate (III) and valerate (V). The amount of copper used as catalyst and the rate of heating varied, but in all cases the discontinuity at  $280^{\circ}\text{C}$ . is pronounced and appears independently of how the catalyst is made. The same observation was made for copper activated by ammonia (fig. 1, Curve V).

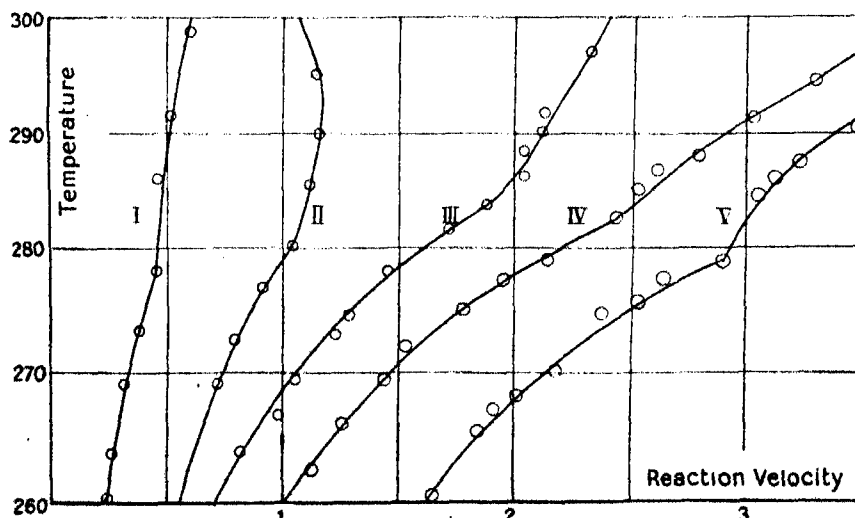


FIG. 5, showing that poisoning by the reaction products commences about  $280^{\circ}\text{C}$ . independently of the method of preparation of the active copper.

*Discussion of Results.*

The copper surfaces obtained by electrolytic deposition, the reduction of ammoniacal solutions of copper, and by hammering and polishing were found to be inactive as catalysts. Produced by the rapid condensation of copper vapour, or by the violent agitation of the atoms in an inactive surface at  $820^{\circ}\text{C.}$ , or by the thermal decomposition of copper salts in a rapid stream of indifferent gas, they were found to be active. The inactive forms presented a bright metallic appearance, and the surface as seen under the microscope was quite smooth, the surface activity per unit area being at most  $1/20\text{th}$ , and probably less than  $1/5000\text{th}$ , that of reduced copper.

Palmer\* suggested that the inactivity of electrolytic copper was due to its being composed of cupric-copper atoms, and further, extended the hypothesis to account for the variation of the activity of reduced copper with the temperature of reduction and the reducing agent used. It has, however, been shown that the activity of preparations of copper from cuprous and cupric oxides are almost equal—hence this theory becomes untenable. Adkins† has advanced an alternative explanation: "Copper ions when discharged at the electrode are free to take up positions which will most completely satisfy the secondary fields of force about the copper atoms. This means that the copper atoms will be closely packed, and there will be a weak field of force at the surface." This theory is confirmed by the present work, and can be applied to the explanation of the inactivity of the other preparations.‡ Beilby suggested that polished metals were covered with a vitreous flowed layer. X-ray analysis has shown that these layers are crystalline, and probably differ from the mass of the metal only in the size of the crystal grains.§ The flow of the surface atoms would occur, leaving the smallest possible stray field. It is interesting to notice that Bennett|| states that electrolytically deposited copper does not differ materially in properties from cast copper having the same size of crystals.

The metal produced by the catalytic decomposition of ammonia at  $820^{\circ}\text{C.}$  was a dull yellow colour, the surface being deeply pitted. It was found that the activity of this preparation was constant for some hours, yet on re-exami-

\* 'Roy. Soc. Proc.,' A, vol. 98, p. 23 (1920), vol. 99, p. 420 (1921).

† 'J. Amer. Chem. Soc.,' vol. 44, p. 2185 (1922).

‡ It is essential that the strain be present in the surface-layer of atoms. Strain present in the arrangements of crystal grains beneath the surface naturally has no effect on activity.

§ For discussion see Constable, 'Roy. Soc. Proc.,' A, vol. 107, p. 273 (1925).

|| 'J. Phys. Chem.,' vol. 16, p. 294 (1912).

nation of the copper the metallic appearance had been almost completely regained. Microscopic examination showed that the change was due to the filling up of the larger pits, but the very tiny irregularities on the surface had persisted. We have therefore direct evidence that the surface activity is due to the irregular arrangement of the surface atoms.

The structure of the surface is fixed at the instant of formation, since it has been shown that reduced copper, and metal obtained by thermal decomposition, is uniformly active for many hours.

Catalysts obtained by chemical reaction varied in appearance, from the bright metallic colour of the thin films of copper, through dull yellow, to red-brown powder. With the exception of metal activated by pure ammonia gas and copper produced in a stream of alcohol above 280° C., when the surface is rapidly poisoned by the reaction products, all these preparations showed very nearly the same surface activity and the same temperature coefficient of activity. Between the whole series of measurements there is a fair variation in the "heat of activation," which seems larger than the experimental error.\* A similar variation has been found in the heat of adsorption of hydrogen on various preparations of copper, values ranging from 9600 to 20,000 cal. per gram molecule being obtained,† showing that the effective mean field strengths vary considerably with the state of the surface.

It has, however, been shown that the "heat of activation" measured in heterogeneous catalysis is the value on the most active centres on the surface,‡ and this value does not vary widely with the method of preparation of the catalyst.

When active copper is formed by chemical change the copper atoms are suddenly liberated and crystallize, there still remaining groups of atoms in the surface which are frozen in a state of strain. The fixation of such groups of atoms fixes specific fields of force sufficiently intense to cause such internal strain in the adsorbed molecules that chemical reaction occurs at a measurable rate. Hinshelwood and Pritchard suggest that "When a molecule is adsorbed by a surface the forces between it and the molecules constituting the surface modify the internal forces in a way which is at present entirely incalculable

\* The large variation of temperature coefficient ( $2.00-1.67$ ) found by Palmer ('Roy. Soc. Proc.,' A, vol. 99, pp. 415 and 421 (1921)) has not been confirmed, and it is probable that the high value  $2.00$  is considerably in error, since no cooling curve could be obtained with the technique then in use.

† Beebe and Taylor, 'J. Amer. Chem. Soc.,' vol. 46, p. 43 (1924).

‡ Constable, "The Mechanism of Catalytic Decomposition," 'Roy. Soc. Proc.,' A, vol. 108, p. 376 (1925); 'Proc. Camb. Phil. Soc.,' vol. 22, No. 5, p. 738 (1925).



and must be entirely specific. It would be expected that the stability would be increased as often as it is decreased."\* The paper further considers chemical change as caused by the excessive momentum of parts of the molecule, and justification is given for this mechanical picture in spite of the view that activation consists in the passage of an electron to an orbit of higher quantum number. Norrish† also states: "We may regard molecular activation as occasioned by a definite change of configuration or distortion of the molecule, brought about by close association with some polar catalyst. Such a change must take place with the absorption of energy."

Pease‡ and later Taylor§ attribute catalytic activity to highly unsaturated atoms in the surface. The evidence here given supports this hypothesis, but in view of the fact that the final explanation of chemical phenomena lies in the physical sciences, it seems to be more general to attribute the specific straining of the adsorbed molecule preliminary to chemical reaction to the electrostatic and electromagnetic fields of force on those strained groupings of atoms which constitute the centres of activity of the surface.

In electro-deposition, or in the chemical deposition of copper from solution, the basic space lattice is already present and the slow arrival of the copper atoms enables them to fit into the regular structure, making the external field small. Hammering and polishing apparently do not increase the stray field sufficiently. If the crystalline structure be disturbed, *e.g.*, by the passage of ammonia over the copper at 820° C., the regular arrangement is disturbed and active groupings of atoms are formed and persist in spite of the very high temperature, because of the continuous agitation. The rapid condensation of copper from vapour freezes highly strained arrangements of atoms in the surface, and is consequently active. As the kinetic energy of the atoms of the catalyst increases with temperature, the active configurations slowly change back to the crystalline form. Thus annealing reduces the catalytic activity.

The essential feature necessary to the production of copper catalytically active in the dehydrogenation of alcohols is the sudden liberation of free copper atoms under conditions in which the kinetic energy of the atoms of the structure is insufficient to cause collapse of the active centres. Thus methods of producing copper under the same physical conditions should give copper with the same surface activity and showing the same temperature coefficient. In spite of the wide divergence between the spacing of the copper atoms in copper

\* 'J. Chem. Soc.,' vol. 123, pp. 2725, 2730 (1923).

† Norrish, 'J. Chem. Soc.,' vol. 123, p. 3006 (1923).

‡ *Loc. cit.*

§ *Loc. cit.*

formate and valerate, thermal decomposition gives a product showing very nearly the same temperature coefficient and surface activity.

The measurements also point to the existence of a lower limit to the heat of activation for the given reaction on the catalyst, the variation above this value being only slight. This observation must be taken to mean that there is some limit to the distortion of the adsorbed molecule produced by the centres of activity of one particular substance.

Since the surface fields vary with the nature as well as the arrangement of the surface atoms, the nature and magnitude of the molecular distortion will vary with the chemical nature and the physical state of the surface, and we have an explanation of the specific action of catalysts. It is apparent that very small quantities of added material of suitable physical properties could cause wide variation in the nature and distribution of the centres of activity, and we have a tentative explanation of promotor action. Thus the reaction-centre theory of catalysis is capable of covering a very wide range of hitherto unexplained phenomenon. It is necessary, however, to guard against its application to chemical reactions under conditions in which the continued existence of active spots would be impossible. The persistence of the centres of activity unchanged by chemical reaction requires that the adsorption and desorption of the reactants shall be reversible without alteration of the surface; and that the heat absorption or evolution shall not sinter the existing centres of activity during reaction. Many chemical changes are violent enough to cause marked changes in the surface. In these cases the activity of the surface increases on use to a maximum, which corresponds with the maximum number of centres capable of existing together at a given instant. When the reactants form intermediate compounds with the catalyst the form of the surface is destroyed, and any theory of centres of activity as here formulated cannot be expected to describe the results of experimental work.

My thanks are due to the Department of Scientific and Industrial Research for a grant which enabled this work to be completed.

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### *Fluid Resistance to Moving Spheres.*

By R. G. LUNNON, M.A., M.Sc., Armstrong College, Newcastle-upon-Tyne.

(Communicated by Prof. T. H. Havelock, F.R.S.—Received October 8, 1925.)

The present research was undertaken in order to improve the existing data on the resistance of fluids to moving spheres, and especially to examine the resistance in cases of accelerated motion. Some preliminary results were published in 1924,\* and these are extended in the present paper, which is divided as follows:—

- I. Experimental.
- II. Equations of motion.
- III. Analysis of results—
  - A. For terminal speeds.
  - B. For initial stages of acceleration.
  - C. For final stages of acceleration.
  - D. For all values of acceleration.
- IV. Comparison with previous work.
- V. Special notes, and summary.

#### *I. Experimental.*

Spheres have been allowed to fall under gravity through a large number of different distances, some within buildings of Armstrong College, Newcastle, and some in certain coal-mine shafts in the Tyneside district. Time measurements have been made for each of the following distances:—

Within college buildings :  $s = 112\cdot5, 200, 279, 337, 380\cdot4, 563\cdot5, 787, 1694$  cms., and others.

In college tower and chimney-stack :  $s = 20\cdot05, 35\cdot70, 36\cdot85$  metres.

In Blucher pit :  $s = 17, 35\cdot1, 55\cdot2, 73\cdot5, 91\cdot7, 110, 126$  metres.

In Usworth pit :  $s = 61\cdot9, 116\cdot8, 180\cdot8, 247\cdot3, 309$  metres.

In Hebburn pit :  $s = 320$  metres.

In Wearmouth pit :  $s = 49, 86, 346, 546, 568$  metres.

In Silksworth pit, Sunderland :  $s = 538\cdot5$  metres.

These distances were measured in most cases with a 100-foot steel tape ; in others, they were taken from the mine surveyor's plans.

\* Lunnnon, 'Phil. Mag.,' vol. 47, p. 173 (1924).

The spheres used have been of wax, wood, stone, rubber (hollow and solid), and steel, and varied from 0·2 to 10·2 cms. in diameter. In the case of steel, a wide range of accurate spheres was available, as made for ball bearings. (See Table VIII.) Sixty assorted spheres of other materials were used, but there was no regular variation of mass or size among these, as repeated losses occurred under the difficult conditions unavoidable in some of the pit shafts; the reduction of the results presented greater difficulties in consequence of this lack of regularity.

The times taken for the spheres to fall through each of these distances were measured by means of a chronograph or a stop-watch. The record was usually an automatic one—the ball being released from an electromagnetic holder, and caught on a special board or card, so suspended by a spring that an electric current was interrupted at the instant of striking. Some of the balls were too light or too small to record their arrival at the foot of the shaft in this way, and a stop-watch, reading to 1/100 second, was then used. In some cases, too, it was not possible to instal the electrical circuits, and the balls were dropped and timed by hand.

If a steel ball is held in direct contact with an electro-magnet, there is a time-lag between the stopping of the current and the release of the ball and this varies with the weight of the ball. In these experiments, therefore, the ball was carried on a light wire ring, which projected from a hinged arm carrying the heavy keeper of the magnet. A thin card prevented the keeper from coming into contact with the core of the magnet; and the weight of the keeper was so large in comparison with the weight of the ball that the lag did not vary for different balls. The ring support was adopted after trials with other methods, on the grounds of its interfering least with the stillness of the air in which the ball began its fall.

The time measurements in the early experiments were made on the smoked paper of a drum-chronograph, holes being made in the paper by sparks from a small induction coil at the instants of release and striking. Some lag was introduced through the relays in the electrical circuits, and this was accurately measured by a special series of experiments; its value in one case was 0·036 seconds. But the drum-chronograph proved to be unequal to the task of measuring intervals of several seconds to the nearest 1/1000 second, and the whole of this work was repeated when a phonic dial chronoscope became available. In this instrument, which has been described by Wood,\* the rating

\* A. B. Wood, 'Jour. Sci. Instrum.', vol. 1, p. 161 (1924).

depends upon the vibrations of an electrically-maintained tuning fork, governing a phonic motor ; the electric current is always adjusted to the same value, and a separately-determined correction is made for variations of temperature. As an example of the concordance of the readings obtained with this chronoscope, we record a set of seven consecutive times taken by seven steel spheres, each of mass 24·67 grams and diameter 1·83 cms., in falling through 35·70 metres.

2·781, 2·784, 2·786, 2·782, 2·784, 2·784, 2·782 seconds.

This precision was not always reached, but the values recorded in Tables I and II are believed to be correct within 0·002 second for all the distances up to 3,600 cms. For greater distances, the results for steel spheres are more accurate than those for other balls, because they represent in every case the mean of five separate readings ; the errors do not exceed 0·02 second for times up to 6 seconds, and 0·1 second for longer falls. The figures for other spheres are also mean values in some cases ; in others they are single readings, and may be 0·1 second in error for the lightest balls.

On some days when mine shaft measurements were attempted, it was not possible to arrange for the artificial ventilation of the pit to be stopped ; and in two pits there remained a natural draught, although the driving fan was stopped. It was then necessary to make measurements of the wind-speed at various points in the shaft, using an anemometer. There were other practical difficulties. Few pit shafts are completely dry, and sometimes there was so much water dropping in the shaft that many attempted readings were spoiled. The cases in which balls had collided with water-drops in their descent were easily detected by the divergence of their times from the mean, and only those results were used, and are here recorded, which were shown to be reliable by repetition or by comparison with other results. Fortunately in the Hebburn and Silksworth shafts there was complete dryness and almost complete stillness ; in the Usworth pit there was very little water and a regular up-draft for which corrections could be definitely made. (The Wearmouth records suffered from all the disadvantages, and also from the presence of side-draughts at levels in the shaft where side-galleries opened into it. It proved to be impossible to interpret the readings obtained, so that here the labour of installing apparatus, including three-quarters of a mile of wire, was in vain.)

A selection of about one-third of the final results is given in Tables I and II. They are the experimental readings in still air, except for the figures in brackets, which record the results against a draught and also the corrected times. There are some small experimental errors in the figures : they are readily seen on

analysis, and may be corrected by comparison with neighbouring figures, and with others not included in these shortened tables. It is not convenient to exhibit these results graphically as  $s, t$  curves, because the times differ so little from the times that would be obtained in a vacuum that the curves would be crowded together. They are more clearly separated by plotting  $s - 20t$  against  $t$ , as is shown in our previous paper,\* and still better by plotting  $t - t_0$ , the time retardation against  $t_0$ , where  $t_0$  is the time *in vacuo*, given by  $s = \frac{1}{2}gt_0^2$ . Some curves of the latter kind are shown in fig. 1. Curves of this kind, on a larger scale, have been specially used in dealing with the much more accurate

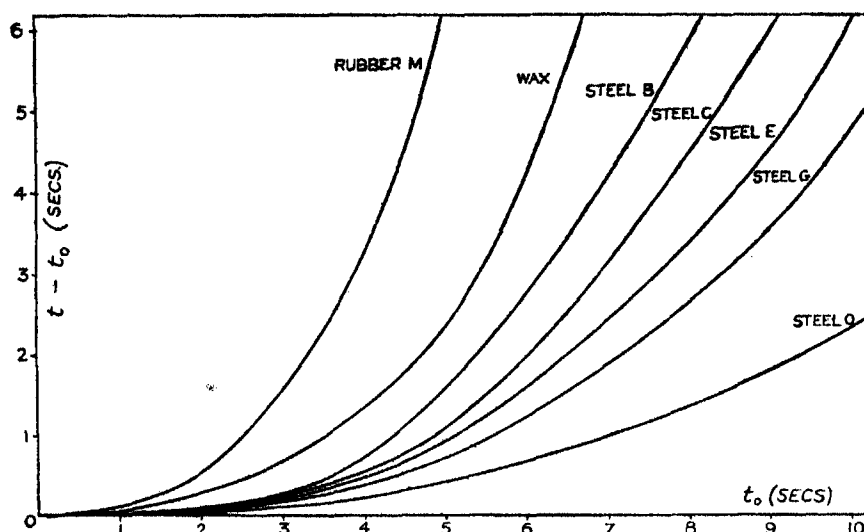


FIG. 1.—To show increase of time retardation ( $y$ ), with increase of time of free fall ( $t_0$ ) *in vacuo* for seven spheres.

results for the falls through the eleven smallest distances ; four of these sets of results are at the head of Tables I and II.

*Atmospheric Conditions, etc.*—The density, temperature and humidity of the air were not constant throughout these experiments. At the foot of the Hebburn shaft (320 metres) the temperature and pressure were  $23^{\circ}\text{C.}$  and 818 mm., whilst the relative humidity was measured and found to be 0.74 ; the density was therefore 0.00127 grms. per c.c. In the Silksworth pit temperature and pressure increased from  $12^{\circ}\text{C.}$  and 752 mm. at bank to  $22^{\circ}\text{C.}$  and 806 mm. at 538 metres depth, with relative humidity rising from 0.32 to 0.60. The change in density was therefore an increase from 0.00121 to 0.00127.

\* Lunnion, 'Phil. Mag.,' vol. 47, p. 173 (1924).

Table I.—Times of Fall of 9 Steel Balls, together with Times *in vacuo*,  $t_0$ .

Letter.	B.	C.	E.	G.	K.	M.	N.	O.	
$m$	0.129	0.432	1.03	2.69	5.57	9.89	15.16	24.67	grams
$d$	0.317	0.476	0.635	0.873	1.11	1.35	1.55	1.83	cms.
$24 \frac{\sqrt{m}}{d}$	27.1	33.1	38.3	45.0	50.9	55.8	59.7	65.1	metres per second.
$s$ Metres.	$t_b$	$t_c$	$t_e$	$t_g$	$t_k$	$t_m$	$t_n$	$t_o$	$t_0$ Seconds.
3.37	0.840	—	0.839	—	0.835	0.834	0.832	0.831	0.829
7.87	1.304	1.298	1.295	1.292	1.290	1.287	1.284	1.270	1.267
16.94	1.97	1.94	1.926	1.920	1.912	1.906	1.903	1.898	1.859
35.70	2.05	2.89	2.87	2.853	2.837	2.805	2.792	2.783	2.698
55.2	3.76	3.67	3.61	3.57	3.54	3.52	3.50	3.48	3.35
73.5	4.51	4.35	4.25	4.21	4.15	4.11	—	4.06	3.87
91.7	5.22	4.98	4.92	4.80	4.70	4.66	—	4.59	4.32
110	5.93	5.62	5.43	5.38	5.22	5.17	—	5.09	4.74
128.1	6.67	6.17	5.93	5.78	5.67	5.59	—	5.51	5.07
(180.8)	—	(7.80)	(7.28)	(6.95)	(6.81)	(6.74)	(6.71)	(6.60)	—
180.8	—	8.45	7.80	7.35	7.05	6.90	6.82	6.75	6.07
(247.3)	(9.87)	(9.37)	(8.86)	(8.45)	(8.24)	(8.02)	(7.94)	(7.80)	—
247.3	11.10	10.33	9.42	8.98	8.60	8.33	8.21	8.02	7.10
320	14.00	12.55	11.40	10.71	10.20	9.88	9.76	9.30	8.08
538.5	22.03	19.20	17.46	15.88	14.67	—	13.45	12.87	10.48

Most of our terminal velocity measurements were made in the lower part of this pit, and hence we take 0.00125 as the appropriate value of the density  $\rho$ . The effects of these variations upon the values of the terminal velocity are less than one per cent. Our analysis of the accelerated velocities for the early portions of the falls is necessarily limited in exactness by these variations of density. As a result of the measurements made (as above) during each set of experiments we take 0.00127 as the mean value of  $\rho$  for this section of the work.

The viscosity of dry air increases from 0.000180 at 15° C. to 0.000184 at 23° C.; and there appear to be no reliable records of its value for damp air.\* The figure for water vapour at 15° C. is 0.000097, and such indications as are available†‡ point to the effects of small amounts of vapour in the air being negligible.\* We have therefore taken the value 0.000183 for our analysis, and for the kinematic viscosity ( $\eta/\rho$ ) we have  $0.000183 \div 0.00125 = 0.146$ .

\* We have since found one recorded measurement, by Zemplén, in 'Ann. Physik,' vol. 29, p. 869 (1909). There appears to be an anomalous increase of viscosity, by 0.8 per cent., when air becomes saturated with water vapour, and if this is true our values of R (Reynold's number) should be diminished by this amount.

† Pederen, 'Phys. Rev.,' vol 25 (1907).

‡ Wiedemann, 'Handbuch,' vol. 1, p. 2.

Table II.—Times of Fall of 11 Spheres, compared with Times of Fall in *vacuo* (last column).

—	Rubber M.	Wood. A.	Rubber. O.	Rubber. C.	Wax.	Rubber. R.	Wood. R.	Wood. B.	Wood. C.	Stone. W.	Stone. M.	—
<i>m</i>	32.3	4.12	78.3	38.2	2.92	13.0	10.32	16.57	43.2	12.1	74.0	grams.
<i>d</i>	10.2	2.48	9.4	6.54	1.80	3.75	3.09	3.72	5.10	2.25	3.80	cms.
$24\sqrt{m}/d$	13.4	19.6	22.6	22.6	22.8	23.0	25.0	26.3	31.0	37.1	54.3	metres per sec.
Metres. 3.37	Seconds. 0.886	0.853	0.848	0.847	—	0.844	0.838	0.838	0.835	0.833	0.833	Seconds. 0.829
7.87	1.419	1.330	1.325	1.316	—	1.318	1.305	1.305	1.302	1.295	1.291	1.267
16.94	2.343	2.080	2.059	2.051	2.05	2.049	2.014	2.002	1.977	1.950	1.923	1.859
35.70	4.164	3.20	3.254	3.260	3.26	3.257	3.164	3.143	3.057	2.90	2.822	2.698
55.2	—	—	4.45	—	—	—	—	3.95	3.82	3.56	—	3.35
110.0	9.62	7.1	—	6.75	6.90	—	6.13	—	—	—	5.19	4.74
180.8	—	—	—	10.35	10.50	—	—	—	8.64	7.96	7.10	6.07
247.3	—	—	—	—	—	—	—	—	—	9.80	8.63	7.10
320.0	—	—	—	—	17.2	17.5	16.0	15.1	13.6	—	—	8.08
538.5	—	30.25	—	26.2	27.4	26.8	25.1	23.35	20.82	17.6	15.0	10.48



The increase of  $g$  with depth does not affect the present results. The value increases by 0.005 per cent., in descending 400 metres, and  $t$  is therefore only reduced by about one half as much as this. It may be noted that Airy's measurements of  $g$  were carried out in the neighbouring Harton pit.

The deviation of the line of fall from the perpendicular should not be more than a few inches at the foot of the longest shaft, and has no appreciable influence on the present time-readings.\* The only observations of this deviation in a deep pit are those recorded by Rundell,† in 1847: and he notes only that, in a fall of 400 metres, a few of the balls were deviated from 10 in. to 20 in. to the south. It was impracticable to make measurements of this quantity in the present experiments.

## II. Equations of Motion.

The motion of a falling body is represented by the equation

$$m\dot{v} = m'g - F, \quad (1)$$

where  $m$  is the mass of the body,  $m'g$  its weight in the surrounding fluid, and  $F$  the fluid resistance. In the present experiments we take  $m' = m$ , as the spheres concerned are all very much heavier than air. When the influence of acceleration is neglected, it is usual to write

$$F = \psi \rho d^2 v^2, \quad (2)$$

where  $\rho$  is the fluid density and  $d$  is the diameter of the body, in this case a sphere. The number  $\psi$  is of zero dimensions, and its variation is a special subject of study: we shall call it the *resistance coefficient*. It is usually compared with the number  $R$  also of zero dimensions, which is given by  $vd/\nu$  and corresponds to the *Reynolds number* for flow in pipes. (The quantities  $\psi$ ,  $R$  have been sometimes denoted by  $\phi_1$ ,  $\phi_2$ , and  $\psi$  is the drag-coefficient.)

Substituting (2) in (1) and integrating we find

$$v = c \tanh pt \quad (3)$$

where

$$c = \sqrt{\frac{mg}{\psi \rho d^2}}, \quad \text{and} \quad p = \frac{g}{c} = \sqrt{\frac{\psi g \rho d^2}{m}}. \quad (4)$$

The constant  $c$  is the final or terminal speed of the falling body.

The distance fallen in  $t$  seconds is

$$s = (c/p) \log \cosh pt. \quad (5)$$

\* Cf. Baker, 'Phys. Rev.', vol. 14, p. 352 (1919).

† Rundell, 'Proc. Cornish Polytech. Soc.', p. 28 (1847).

To allow for the effect of acceleration, we have previously suggested the formula

$$F = \psi \rho d^2 v^2 - b \dot{v}. \quad (6)$$

This leads to

$$(m + b) \dot{v} = mg - \psi \rho d^2 v^2, \quad (7)$$

from which

$$v = c \tanh qt, \quad s = (c/q) \log \cosh qt$$

where

$$c = \sqrt{\frac{mg}{\psi \rho d^2}}, \quad \text{and} \quad q = \sqrt{\frac{\psi \rho d^2 mg}{m + b}}, \quad (8)$$

and the relation between  $c$  and  $q$  is

$$\frac{1}{q} = \frac{c}{g} + \frac{b}{\psi \rho d^2 c}. \quad (8A)$$

The connection between velocity and distance is

$$v^2 = c^2 (1 - e^{-q^2 t^2}). \quad (9)$$

In a fluid of density  $\rho'$  the expressions are similar, and  $c, q$  are replaced by  $c', q'$ , where

$$c' = c \sqrt{\frac{\rho}{\rho'} \left(1 - \frac{\rho'}{\delta}\right)}, \quad q' = q \sqrt{\frac{\rho}{\rho'} \left(1 - \frac{\rho'}{\delta}\right)}, \quad (10)$$

and  $\delta$  is the density of the falling sphere.

*Approximate Expressions.*—(a) It is useful to note the time and distance at which the velocity does not differ by more than one per cent. from the terminal velocity,  $c$ . Since  $0.99 = \tanh 2.65$ , these are given by  $t = 2.65/q$  and  $s = 1.96 (c/q)$ . If  $b = 0$ , they become  $t = 0.27 c$ ,  $s = 0.20 c^2$ , and if  $b = \frac{1}{2}m$  they are  $t = 0.40 c$ ,  $s = 0.30 c^2$ , the speeds and distances being measured in metres. For example, a steel ball of 1.83 cms. diameter, falls nearly 480 metres before attaining 99 per cent. of its terminal speed.

(b) For long distances of fall, for which  $t$  is large, we may write  $\frac{1}{2}e^{qt}$  for  $\cosh qt$ , and it follows that

$$s = ct - (c/q) \log 2 = ct - 0.69 (m + b/\psi \rho d^2). \quad (11)$$

This formula was first used by Newton, who took  $b = 0$  and  $\psi = (\pi/16)$ .

(c) For very short falls, when  $qt$  is small compared with unity, it is easily shown that an approximate formula is

$$s = \frac{1}{2}cq^2 t^2 - \frac{5}{24}cq^3 t^4.$$

The second term shows the effect of the air resistance upon the distance ;

and the effect upon the time taken for any given  $u$  distance is shown by the expression :—

$$t = t_0 + \frac{t_0}{12m} (6b + 5\psi\rho d^2s).$$

For  $s = 123$  cms., this expression indicates an increase in time of 0.02 seconds for a steel ball of 1.55 cms. diameter.

It is further necessary to consider the equations of fall in a current of air, in order to apply corrections to the experimental results obtained when the air was not at rest. If the fall is opposed by an upward wind of velocity  $u$ , the conditions are expressed by

$$(m + b) \dot{v} = mg - \psi\rho d^2 (v + u)^2. \quad (12)$$

It follows that

$$s = \frac{c}{q} \log \frac{1 + re^{2qt}}{1 + r} - (c + u) t \quad (13)$$

where

$$r = (c + u)/(c - u).$$

When the current is downward, it helps the ball until the ball is travelling just as fast as the wind. This period is brief if the draught is slight; we have

$$(m + b) \dot{v} = mg - \psi\rho d^2 (u - v)^2 \quad (14)$$

and therefore

$$v = u - c \frac{u - c \tan qt}{c - u \tan qt} \quad (15)$$

so that if  $T$  seconds elapse before  $v = u$ , and  $T$  is small, then

$$T = \frac{u}{cq}.$$

To find the distance travelled in this time, it is only necessary to integrate an approximate form of (15) and this leads to

$$S = \frac{1}{2} cqT^2.$$

After this stage, the ball continues to fall in the way already described, and the expression for the total distance travelled in time  $t$  is

$$s = (c/q) \log \cosh q(t - T) + u(t - T) + S. \quad (16)$$

It has been necessary to use equations (13) and (16) frequently, although their form makes the calculation of  $t$ , for given values of  $s$ ,  $c$ , and  $q$ , very laborious. In correcting any observed result it is necessary to assume values of  $c$  and  $q$  to begin the calculation, although the correct values of  $c$  and  $q$  are ultimately to be re-calculated from the results. This is not a serious drawback, however,

for approximate values are sufficient in these small corrections, and these are provided by the numerous independent results. To illustrate the order of these corrections—which are also shown in Tables I and II, we give a Table (IV) showing the effect of air currents in helping and in hindering the fall of a steel ball of diameter 1.11 cms., as calculated from these equations.

Table IV.—Showing effect of air-draughts in the distances travelled in different times.

Times of fall	2	4	6	8	10	12 seconds.
In still air	17	65	134	220	312	410 metres.
Against 1.8 m.p.s.	16.5	64	132	214	303	398 "
With 4.8 m.p.s.	18	66	140	238	333	443 "

### III. Analysis of Results.

A. *Terminal Speeds.*—The mean velocities in the various intervals shown in Tables I and II have been calculated from the distances and times, and the velocities have also been determined graphically from the curves of  $t - t_0$ ,  $t_0$ . It appears that the heaviest steel balls were still gaining speed after falling through 320 metres, and it is not possible therefore to deduce with certainty their terminal velocities from our readings. For a selection of the other balls, with which terminal speeds were proved to have been reached, the results are given in the following table. (Table V.)

Table V.—Terminal speeds for 13 spheres with values of resistance coefficient,  $\psi$ , and Reynolds number, R.

	$d$ cms.	$v$ metres/ sec.	$F = mg$ dynes.	$\psi$ .	R.
Rubber M	10.2	13.6	$31.7 \times 10^3$	0.131	$9.50 \times 10^4$
Wood A	2.48	18.7	$4.04 \times 10^3$	0.143	$3.25 \times 10^4$
Wax	1.80	21.4	$2.84 \times 10^3$	0.162	$2.60 \times 10^4$
Rubber C	6.54	22.6	$37.5 \times 10^3$	0.137	$10.1 \times 10^4$
Rubber R	3.75	23.5	$12.9 \times 10^3$	0.131	$6.0 \times 10^4$
Wood R	3.09	24.0	$10.12 \times 10^3$	0.147	$5.1 \times 10^4$
Wood B	3.72	26.5	$16.26 \times 10^3$	0.134	$6.76 \times 10^4$
Wood C	5.10	30.1	$42.4 \times 10^3$	0.143	$10.5 \times 10^4$
Stone W	2.25	37.3	$11.9 \times 10^3$	0.135	$5.75 \times 10^4$
Steel B	0.317	27.2	$0.127 \times 10^3$	0.136	$0.69 \times 10^4$
Steel C	0.476	32.9	$0.424 \times 10^3$	0.138	$1.07 \times 10^4$
Steel E	0.635	37.3	$1.020 \times 10^3$	0.145	$1.62 \times 10^4$
Steel G	0.878	42.3	$2.640 \times 10^3$	0.154	$2.63 \times 10^4$

The number  $\psi$  is also calculated in each case, and its values are shown graphically later, in fig. 7. They show a steady increase from 0.136 to 0.154 for the first four of the series of steel balls: and if the series were continued to the heavier balls, the indications are that the value of  $\psi$  would again decrease. For the other balls, there is no regular variation of the coefficient. For them the values of  $R$  are greater, and there is a tendency for  $\psi$  to diminish slightly as  $R$  increases.

It may be noted that (8) may be written:

$$c = \sqrt{(g/\psi\rho)} \cdot \sqrt{(m/d)},$$

and as the variations of  $\psi$  from the value 0.132 are small, the formula

$$c = 24\sqrt{(m/d)} \text{ metres per second}$$

is a very good approximation to the terminal speed of any ball. This is illustrated in fig. 2, where the measured values of  $c$  are plotted against those of  $24/\sqrt{(m/d)}$  for a score of different balls.

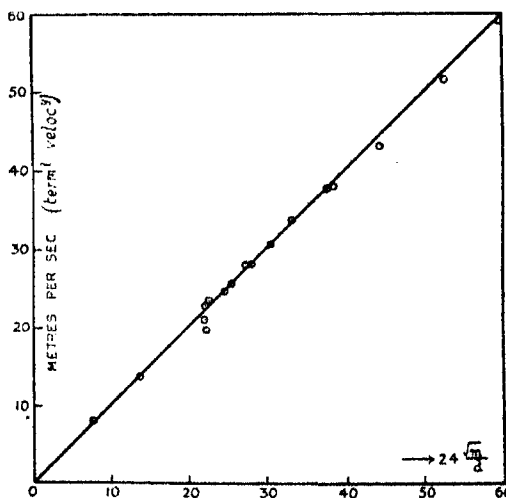


FIG. 2.

**B. Accelerated Motion, Early Stages.**—The early stages of the falls are very well represented by the  $(t - t_0, t_0)$  graphs, and these are of so much greater curvature than the  $(s, t)$  graphs that their superiority for the exact measurement of velocities is evident. The derivatives have been accurately measured, and from their values further curves have been drawn and the second derivatives measured.

If we write

$$y = t - t_0 = t - \sqrt{\frac{2s}{g}}$$

it follows that

$$v = gt_0 (1 - \dot{y})$$

and

$$\dot{v} = g (1 - \dot{y})^2 - gt_0 \ddot{y}.$$

Also, since

$$m\dot{v} = mg - F$$

we have

$$F = mg (2\dot{y} - \dot{y}^2 + t_0 \ddot{y}). \quad (17)$$

For six spheres, the values of  $F$  have been calculated from this expression, using the first and second derivatives of  $y$ . The method is accurate in practice, but we have not relied solely upon it, and have obtained more complete results by the converse process described below.

A connection was next sought between  $F$ ,  $v$  and  $\dot{v}$ , and it appeared, surprisingly, that  $F$  is very nearly a linear function of  $v^2$  for about the first three seconds of fall. The graphs of  $F$ ,  $v^2$  for these first spheres are shown in fig. 3; actually,  $F/mg$  is plotted against  $v^2/g^2$ .

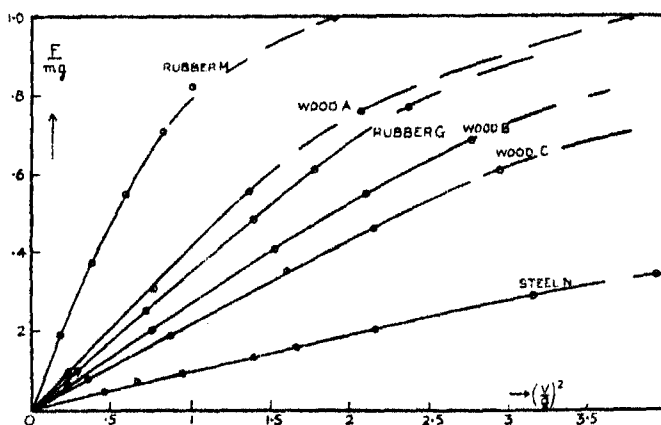


FIG. 3.

These curves are well represented in their early stages by a linear relation between  $F$  and  $v^2$

$$Fg = kmv^2, \quad (18)$$

and the values of  $k$  are as follows :—

Steel N.	Wood C.	Wood B.	Rubber G.	Wood A.	Rubber M.
0.090	0.21	0.25	0.34	0.41	0.90
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This ratio of  $F$  to  $v^2$  is very different from the same ratio when terminal speeds have been attained: in these first stages, on account of the acceleration, it has a very high value. Thus for the light ball, rubber M, we find  $F = 0.027 v^2$  for the first few seconds of fall, then for a period  $F$  is not proportional to  $v^2$ , and finally, when the speed is steady,  $F = 0.017 v^2$ .

As a check upon these values of  $k$  we have calculated back from them to the values of  $y$ , and these are compared in Table VI with the experimental values of  $y$ .

We have shown in equations (2), (4) and (5), that if  $F = av^2$ , then

$$s = \frac{m}{a} \log \cosh t \sqrt{\frac{ag}{m}} \quad \text{or} \quad t = \sqrt{\frac{m}{ag}} \cosh^{-1} e^{(as/m)}.$$

Hence it follows from (18) that

$$t = \frac{1}{\sqrt{k}} \cosh^{-1} e^{(ks/g)}, \quad \text{whilst} \quad t_0 = \sqrt{\frac{2s}{g}}.$$

The differences,  $y$ , between  $t$  and  $t_0$ , have been calculated from these expressions.

Table VI.—Experimental Values (E) and Calculated Values (C) of Time Retardations for Six Spheres.

Sphere.	$k$ .	Time $t_0 =$	0.8 secs.	1.00	1.80	2.60	3.00 secs.
Steel N	0.090	E	0.008	0.010	0.048	0.108	0.162 secs.
		C	0.004	0.007	0.040	0.117	0.172 secs.
Wood C	0.212	E	0.007	0.018	0.093	0.241	0.340 secs.
		C	0.009	0.017	0.091	0.240	0.340 secs.
Wood B	0.255	E	0.008	0.020	0.106	0.280	0.392 secs.
		C	0.011	0.020	0.106	0.275	0.392 secs.
Rubber G	0.336	E	0.013	0.028	0.136	0.334	0.465 secs.
		C	0.013	0.027	0.134	0.331	0.470 secs.
Wood A	0.410	E	0.021	0.033	0.151	—	0.550 ? secs.
		C	0.017	0.031	0.154	0.380	0.530 secs.
Rubber M	0.90	E	0.041	0.070	0.270	0.600	0.800 secs.
		C	0.035	0.064	0.274	0.611	0.810 secs.

The agreement is very good ; so that the graphically determined values of  $k$  are good ; and it remains to discover the meaning of the new constant  $k$ . With this object, we have first evaluated  $k$  for twelve other spheres, which have not been treated above because the time-records were too few for the  $yt$  curves to be drawn. The method of the last paragraph has been used to find  $k$  in these cases : the retardation,  $y$ , was calculated for a number of different values of  $k$ , and those values were selected which gave the best accord with experiment. The complete results are given in Table VII ; the number of experimental readings on which the deduction of  $k$  is based is recorded also ; there were generally about six readings, resembling those of Table VI for each sphere.

Table VII.

Sphere	$k$	$0.3 d^2/m$	No.
Rubber M .....	0.90	0.97	9
P .....	0.44	0.40	4
Wood A .....	0.41	0.44	6
Rubber S .....	0.37	0.32	4
G2 .....	0.36	0.36	9
O .....	0.35	0.34	7
Q .....	0.34	0.32	5
C .....	0.34	0.34	7
G .....	0.34	0.34	6
G1 .....	0.32	0.32	5
SR .....	0.32	0.32	8
Wood R .....	0.27	0.27	5
B .....	0.25	0.25	7
C .....	0.21	0.19	7
Steel E .....	0.12	0.11	5
N .....	0.09	0.05	11
Stone M .....	0.08	0.07	5

It appears that the value of  $k$  is approximately given by  $k = 0.3 d^2/m$ . On combining this with (17), we obtain the following simple law for the resistance to the accelerated motion of fall during the first three seconds :—

$$F = 0.00031 d^2 v^2. \quad (20)$$

Of course  $F$  is actually a composite function of  $v$  and  $\dot{v}$ , and  $\dot{v}$  is only absent in this equation because it is expressible as a linear function of  $v^2$ .

C. *Later stages of accelerated Motion.*—Attempts to continue the methods of the last section to the results of longer falls have shown that there are not enough time readings to allow of equally accurate deductions. It is, however, possible to obtain a useful approximate formula in another way. (This has



been described in a previous paper.\*) We have taken the previous relation

$$s = c/q \log \cosh qt,$$

and have found by trial, for each ball, those values of  $c$  and  $q$  which give the best fit with the experimental values of  $s$  and  $t$ . The results are given in Table VIII. The values are not so connected as to make  $cq$  a constant, as they would

Table VIII.—Dimensions and Constants for Steel Balls.

Reference Letter.	Diameter (cm.).	Mass (grams).	(Terminal velocity) (cm. per sec.).	$q$ (sec. <sup>-1</sup> )	$b$ (grams).
A	0.238	0.054	2350	0.54	0.031
B	0.317	0.129	2710	0.51	0.055
C	0.476	0.432	3310	0.461	0.124
D	0.555	0.602	3590	0.439	0.169
E	0.635	1.03	3830	0.422	0.22
F	0.714	1.47	4070	0.406	0.28
G	0.873	2.69	4500	0.378	0.42
H	0.952	3.48	4700	0.366	0.50
I	1.03	4.44	4900	0.354	0.58
K	1.11	5.57	5090	0.343	0.68
M	1.35	9.89	5580	0.319	1.00
N	1.55	15.16	5970	0.301	1.32
L	1.65	18.25	6180	0.293	1.50
O	1.83	24.67	6510	0.280	1.83

be if the law  $F = av^2$  held good. (See equations 2, 4 and 5.) But they are related in this manner :—

$$1/q = Ac + B/c,$$

and in equations (6) and (8A) we have shown that this is a consequence of the following law of resistance :—

$$F = av^2 + bv. \quad (6)$$

This law, therefore, is a good approximation to the truth. From the values of  $A$  and  $B$  which thus emerge from the experimental data, we have deduced the value of  $b$  and in Table VIII the values of  $b$  for all the steel balls used are recorded, together with the values of  $c$  and  $q$ . These have been previously published, and we have not re-calculated them from the later completed data because the form (6) is only, as we shall see, a working approximation to the true law. One good proof of their value is the following. Before visiting the Silksworth pit, we calculated the fall times to be expected for the given depth (538.5 metres) from these values of  $c$  and  $q$ , obtained from experiments extending only to 320 metres. They are here tabulated with the observed times :—

\* Lunnion, 'Phil. Mag.,' vol. 47, p. 173 (1924).

Table IX.—Calculated and Observed Times for Fall of 7 Steel Spheres through 538·5 metres.

Sphere.	B	C.	E.	G.	I.	K.	L.
$g$ .....	0·51	0·401	0·422	0·378	0·354	0·343	0·293
$t_{\text{calc.}}$ .....	22·58	19·20	17·30	15·66	14·91	14·54	13·57 seconds.
$t_{\text{obs.}}$ .....	22·03	19·20	—	15·88	15·08	14·67	13·58 „

This is a very satisfactory agreement. There is a regular variation in the discrepancy, which is due to the regular variation in the resistance coefficient having been unrecognised in the earlier data. It is referred to later on p. 321.

D. *Complete course of acceleration.*—Finally, a complete examination of the data for steel balls has been made. The velocities have been found directly from the  $s, t$  readings, by calculating the mean speed in each interval, and the  $v, t$  curve for each sphere has been drawn. Some typical curves are shown in fig. 4.

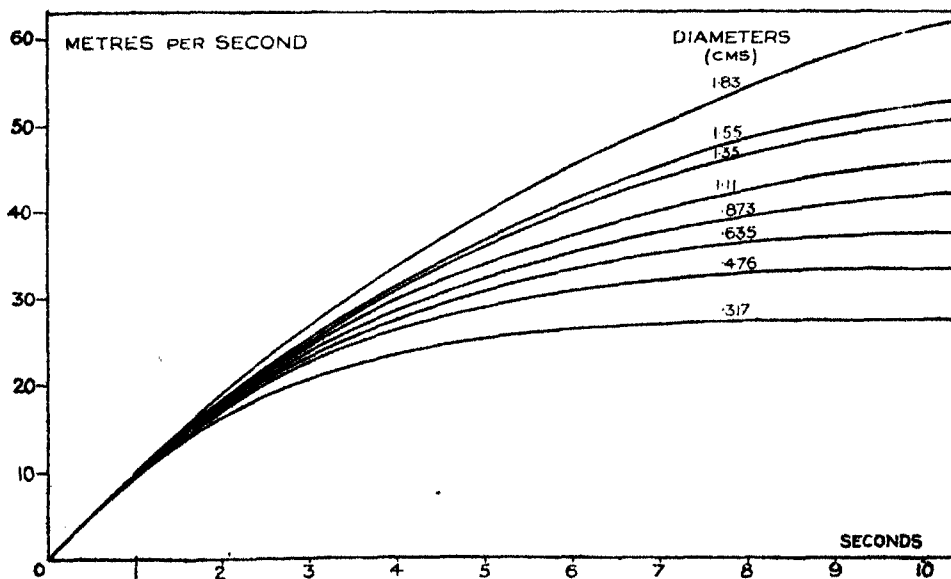


FIG. 4.

From these, the values of the acceleration have been obtained graphically, and the variation of acceleration with velocity throughout the descent of a ball is shown in fig. 5 for eight balls.

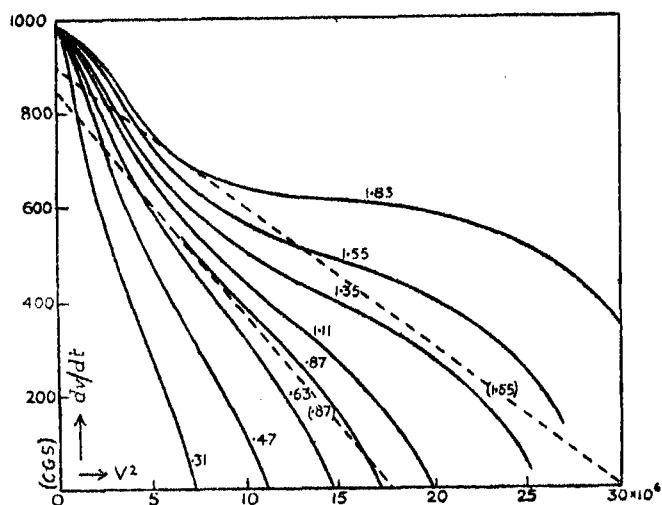


FIG. 5.

Two dotted straight lines are also shown in the figure. These are the lines which express for two of the balls the approximate resistance formula,  $F = av^2 + bv$ , and a comparison of each line with the corresponding curved line shows how far this expression is a useful approximation.

From these curves it is possible to deduce the general manner in which the resistance of a sphere depends upon its velocity and acceleration. Taking any one value of the acceleration, we find for each sphere the velocity at which it is moving when its acceleration has this value, and we calculate also the resistance to its motion at that instant. The relation between the four variables,  $F$ ,  $d$ ,  $v$  and  $\dot{v}$  can be expressed, according to dimensional theory, as a relation between the three derived quantities,  $F/d^2v^2$ ,  $vd$ , and  $\dot{v}d/v^2$ , and their values are next calculated. Then for a constant value of  $\dot{v}d/v^2$ , there should be a curve connecting  $F/d^2v^2$  and  $vd$ . The present readings do not, in fact, yield such a curve—a divergence from theory which is referred to later. They do, however, exhibit a steady variation for constant values of  $\dot{v}$  and the curves connecting  $F/d^2v^2$  (which is proportional to  $\psi$ ) with  $vd$  (proportional to  $R$ ) are given in fig. 6.

The curve for steady motion re-appears in this figure, as the lowest of the series. It is less complete than the others, for reasons already discussed. The other curves show in striking and unexpected way how acceleration increases resistance. They appear to emphasise the most interesting central portion of the usual  $\psi R$  curve (see fig. 7). Their extensions for high values

of  $vd$  suggest that rapid descent of the usual curve, which Eiffel's readings first indicated.\*

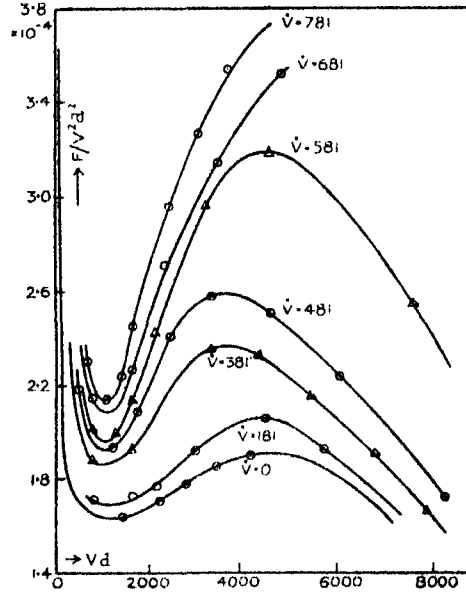


FIG. 6.

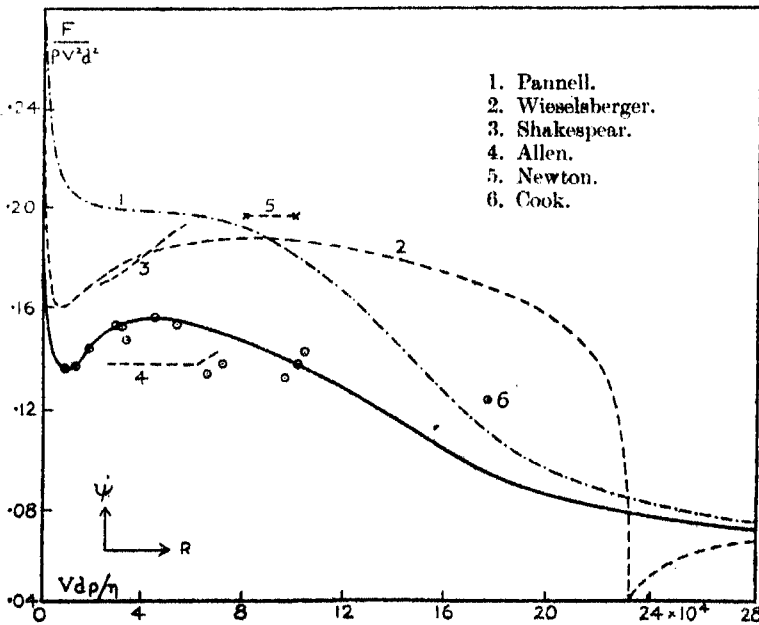


FIG. 7.

\* A similar set cannot be obtained from the results with other spheres summarised in fig. 3, because for them the  $\psi, R$  relation with zero acceleration is not a smooth curve (see fig. 7). The present curves (fig. 6) may be simpler than the most general  $F, v, i, d$  curves, because they are all derived from spheres of the same density.

These curves, like those of fig. 8, can be represented as cubic equations with empirical constants. But the data do not at present make this a profitable step; and it does not appear likely that they will lead to integrable forms in the formulæ for  $v$ ,  $t$  or  $s$ ,  $t$ . The formula (6) remains the best basis for any velocity or distance equations.

It remains to show the contribution of these results to our previous knowledge.

1. *Resistance to Uniform Motion*.—A recent paper by L. F. Richardson\* has summarised most of the available data, and the previous summary by Pannell† showed in greater detail how large were the discrepancies among the results of all experiments carried on in wind-channels. It is clear that widely different degrees or kinds of turbulent motion exist in the different artificial air-draughts used by Eiffel,‡ Pannell,† Prandtl,§ and others, and that the resistance values vary enormously in these conditions, when the velocity is near to a critical value. We have included three of these results in our fig. 7, viz., those published by Pannell from the National Physical Laboratory, those obtained by Eiffel, and the results of the work at the Göttingen Laboratory. We have omitted the results of Zahm,§ which are good for higher values of  $R$ , and also those of Richardson,\* which depend upon an incomplete analysis of accelerated motion. There is good reason, however, for including Sir Isaac Newton's¶ results of 1719, and also one result recorded by Cook.\*\* The recent formula given by Miyagi†† refers only to the non-rigid sphere presented by an air bubble in water.

Newton's results are of much more than historical value, for two reasons. They are obtained from careful experiments which have never been repeated, and they contain a special value for the resistance constant,

$$\psi = \pi/16 = 0.196,$$

which is a remarkably good one, well within the range of modern determinations. Yet it was derived from a theory which appears to have little or no validity; and no subsequent writer has proposed any theory at all. That

\* Richardson, 'Proc. Phys. Soc.,' vol. 36, p. 67 (1914).

† Pannell, 'Adv. Ctee. for Aeronautics Rep. and Mem.,' No. 190 (1916).

‡ Eiffel, 'Comptes Rendus,' vol. 155, p. 1597 (1912).

§ Summarised by Wieselsberger, 'Phys. Zeit.,' vol. 23, p. 222 (1922).

|| Zahm, 'Phil. Mag.,' vol. 1, p. 534 (1901).

¶ Newton, 'Principia,' Book II, Sect. VII, Prop. XL. Excepts. 1-14.

\*\* Cook, 'Phil. Mag.,' vol. 39, p. 350 (1920).

†† Miyagi, 'Phil. Mag.,' vol. 50, p. 113 (1925).

theory led to an expression of the  $s, t$  relation which hardly differs from our own, though its form is different, being based upon the time and distance travelled by the falling sphere, before the terminal velocity is reached. In the experiments two hollow spheres were allowed to fall from the dome of St. Paul's; six were of glass, 13 cm. in diameter and from 30 to 40 grms. in weight. Four were made from hog's bladders, of the same size and one-quarter the weight. The falls were well arranged, and timed to within one-quarter of a second, or less—the total times for about 80 metres ranging to 22 seconds. The agreement of the results with Newton's own theory is good, but not perfect. It can be improved, we find, either by slightly increasing his value of  $\psi$ , or by introducing the acceleration resistance constant  $b$ . The times recorded are just too indefinite to allow of these alternatives being separated; the second is most probably the correct one, and when values of  $b$  have been obtained from future experiments, it will be worth while to analyse the results afresh.

Newton's formula (which is in effect our equation (11)) is

$$s = ct + kc^2(1 + \beta).$$

In one experiment, where  $c = 30$ ,  $t = 8.2$ ,  $\beta = 0$ , this leads to  $s = 75$  metres, which exceeds the experimental value by 2 metres. The correct result follows either by taking  $c = 29.1$ , or by making  $\beta = 0.25$ , or by a combination of these changes. The values of  $\psi$  for these experiments are about  $9 \times 10^4$ .

Thirteen points on the standard  $\psi, R$  graph result from the present experiments (fig. 7). The first five are of the greatest weight, for they represent part of the extensive series of steel ball measurements; they give clear evidence of the range in which the resistance is proportional to a higher power of the velocity than the second. The results from steel balls exceeding 0.87 cm. do not appear in the diagram, because the terminal speeds were not actually reached, and it would be unsafe to extrapolate the curve in this critical range. An examination of the velocity curves in fig. 4 shows, however, that an estimate of the final speeds could be made for these larger balls, and this would indicate clearly that  $\psi$  begins to decrease again. Moreover the success of our initial assumption of a mean value (0.14) for  $\psi$  and the manner in which the variations from this occur, as shown in Table IX, both show that the crest of the curve occurs as we have drawn it in the figure. The results of Shakespear\* and Allen† appear on either side of our own curve. The former's higher values may well be due to the two possible errors which he notes, both

\* Shakespear, 'Phil. Mag.'

† Allen, 'Phil. Mag.,' vol. 50, p. p. 323, 519 (1900).

tending to increase the resistance—the presence of a raised rim on the culluloid spheres, and the non-coincidence of the centre of gravity and centre of figure, leading to slight irregularities of fall. Allen's results in the same range of  $R$  are low; they are inconclusive because the terminal speeds may not have been reached, and because the containing vessel was not very large compared with the falling spheres. They cannot at present be corrected, because Ladenburg's\* vessel-size factor, even as amplified by Oseen and others,† is only applicable for low values of  $R$ .

Our figures for rubber and other balls do not show a regular variation, though they are in general accord with other results, apart from Shakespear's. The points for the largest spheres are far to the right, and they agree well with some observations made by Pannell‡ on a similar sphere exposed to a natural wind. These observations, as shown in his fig. 2, are too numerous and discordant to be shown on our graph, but they surround our three points at  $R = 10^5$ , and show clearly the reduction in air resistance when there is turbulence, as in the present experiments. This reduction has been observed also in the Göttingen aerodynamics laboratory, and it may provide a basis for the measurement of degrees of turbulence. It is to be noticed, however, in applying it to atmospheric turbulence, that the resistance is not only increased by greater stillness in the fluid, but also by any lateral oscillations in the moving sphere, and such movements—of imperceptible amount—are probably set up in all light bodies, such as pilot balloons. They should not occur with smooth heavy spheres.

II. *Resistance to Accelerated Motion.*—There are few published data with which the present results on accelerated motion may be compared. The only extensive examination is that due to Schmidt,§ and is confined to a range of lower values of  $R$ , corresponding to speeds so low that the effects of individual eddies forming behind the sphere are separately noticeable. This stage of the motion lasts for less than one-hundredth of a second in the present cases of free fall in air so that the results are not comparable, except in so far that there is a confirmation of the general increase of resistance on account of acceleration. A few relevant observations have been made by Cowley and Levy|| on a non-spherical body falling in water. We have drawn from their

\* Ladenburg, 'Ann. Physik,' vol. 23, p. 447 (1907).

† A recent summary and test has been recorded by Liebster and Schiller, in 'Phys. Zeitsch.,' vol. 25, p. 870 (1924).

‡ Pannell, 'Adv. Ctee. for Aeronautics, R. and M.,' vol. 190 (1916).

§ Schmidt, 'Ann. d. Phys.,' vol. 61, p. 633 (1920).

|| Cowley and Levy, 'Adv. Ctee. for Aeronautics, R. and M.,' vol. 612 (1918).

results the  $(F/v^2, \dot{v})$  curves corresponding to fig. 6, and they resemble closely the final descending arms of these curves. Further, in the two single cases of fall recorded by Cook and by Allen, we have found that the  $(\dot{v}, v^2)$  curves follow a similar course to those of fig. 5, and in the second case there is exact numerical agreement as well.

The only other record is that made by Shakespeare, who made the important observation that all those spheres for which the ratio  $m/d^3$  is a constant fall at the same rate. The present experiments confirm this over a wide range. For example, the spheres from "Rubber O" to "Rubber R" of Table II range in diameter from 1.8 cm. to 9.4 cm., but their fall times for any distance and the values of  $m/d^2$  are approximately the same. In fig. 8 some actual time

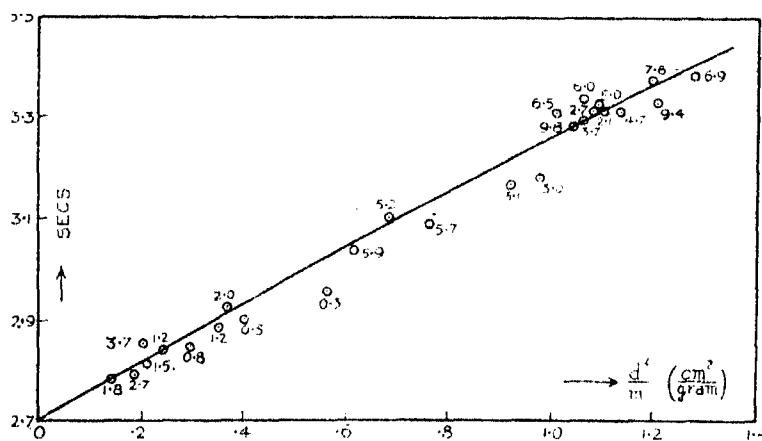


FIG. 8.

readings for a distance of 35.0 metres are shown for 28 spheres; they vary in a regular manner with  $m/d^2$ , and are affected very little by large variations in  $m$  and  $d$ . There may be very slightly less proportional resistance for the smallest balls.

This is not in accord with the indications of dimensional theory. It is easy to show that if the resistance  $F$  depends only on  $v, \dot{v}, d$ , and  $\rho$ , then  $F$  must be expressible in the form

$$F = \rho v^2 d^2 f(vd/v, \dot{v}d/v^2)$$

where  $f$  is an undetermined function. It follows on comparison with (1) that the equation of motion for a falling sphere may be written:

$$m(g - \dot{v})/v^2 d^2 \rho = f(vd/v, \dot{v}d/v^2).$$

The solution of this equation cannot present  $v$  as a function only of  $m/d^2$  unless  $d$  is absent from the unknown function  $f$ . This would be possible if its form



were  $f(\dot{v}/v^3)$ ; but an inspection of the curves will show that  $F/v^2d^3$  cannot be a single-valued function of  $\dot{v}/v^3$ . If it were so, the  $(\psi, R)$  curves of fig. 6 could have been drawn each for a constant value of  $\dot{v}d/v^2$  instead of a constant value of  $\dot{v}$ ; but single-valued curves are not then obtained. The same difficulty appears in another form in our approximate expression for the acceleration—resistance law (Eqn. 6). For the dimensions to be correct, the constant  $b$  must be proportional to the cube of a length (in the case of a non-viscous fluid, this is a well-known result and  $b$  is the dragged mass); but the experimental results are best fitted if  $b$  is proportional to the *square* of the diameter, as in Table VIII. The “dragged mass” is always small in air, and complete observations of the acceleration in a liquid would be helpful in resolving the difficulty. It may well be that the resistance depends also upon the rate of change of the acceleration, and this should be taken as a fifth variable in the dimensional analysis.

The experimental studies of eddy-formation do not at present contribute usefully to the analysis of accelerated motion, except possibly in a point which arises from a comparison of the results of Schmidt with those of Williams.\* These refer to similar values of  $R$ , in the neighbourhood of 1,400, the former for spheres in water, the latter for more slowly moving spheres in viscous fluids. In accelerated motion, Schmidt observed the formation of eddies; in the photographs of Williams, for steady motion, there are no eddies. It is possible that the rapid change in stream-line forms are especially favourable to the production of eddy motion, and that the increase of resistance with acceleration is due to this cause. If so, a negative acceleration may also increase the resistance, and the expression (6) may not be applicable if  $\dot{v}$  is negative. Apart from this, the expression provides a useful further approximation for the solution of special problems in accelerated motion, such as those considered by Littlewood† and by Richardson‡. It has been stated§ that for steady motion the theory of periodic eddies due to Karman is applicable to all values of  $R$  from  $10^2$  to  $10^5$ ; but neither this nor any other theory can at present account for the rise of the resistance coefficient as  $R$  rises from  $10^4$  to  $5 \times 10^4$ . The only clear evidence for periodicity in the eddies is provided by the experiment of Relf and Simmons,|| and it is significant that they record no frequencies in the range  $10^{3.5} < R < 10^5$ .

\* Williams, ‘Phil. Mag.’, vol. 29, p. 526 (1915).

† Littlewood, ‘Proc. Camb. Phil. Soc.’, vol. 22, p. 217 (1924).

‡ Richardson, ‘Phil. Trans.’, A, vol. 223, p. 351 (1923).

§ Wieselsberger, ‘Phys. Zeitschr.’, vol. 23, p. 322 (1922).

|| Relf and Simmons, ‘Rep. Adv. Ctee. Aeronautics,’ No. 917 (1922).

*Spheres with Rough Surfaces.*

On several occasions during the present work, rusty and vaseline-smeared balls were dropped and their times compared with those of smooth spheres of the same size. No perceptible differences appeared when the measurements were made to 1/100 seconds only; but on one occasion a long series of accurate measurements for five different heights was made and a difference appeared. Besides other spheres, ten steel balls of the same size, 0.476 cm. diameter, were dropped from each stage and five rusty ones were dropped alternately with five clean ones. The readings were very consistent, and the results prove that the rusty balls dropped more quickly than the clean ones.

Distance	..	286	797	1035	1373	1692 cm.
Rusty	..	0.7775	1.288	1.466	1.692	1.937 seconds
Clean	..	0.779	1.290	1.467	1.694	1.939 seconds

The time difference is not regular, and it is very small; but its existence is indubitable. The surfaces of the rusty ball were quite rough, though a micrometer gauge recorded no difference in the diameters of the smooth and rusty balls. This observation is in agreement with one recorded by Pannell\* who found the resistance of a 6-inch sphere to be very much reduced by roughening the surface. It is possible that for a rough ball the plane, from which the "wake envelope" begins to leave the sphere, is displaced to the rear of the ball, diminishing the wake cross-section and consequently the resistance. The reduction of resistance which is produced by greater turbulence in the fluid—whether this be due to the initial state of the fluid or to the sphere's own more rapid motion—may be attributed to a similar effect.

*Summary.*

1. Times of fall of spheres from 0.2 to 10.2 cm. diameter through distances up to 538 metres have been measured.
2. An analysis of the motion has provided new data on the variation of resistance with speed and acceleration, in particular—
  - (a) further points are added to the standard  $\psi$ , R curve, and
  - (b) a new series of curves, on the  $\psi$ , R diagram, exhibit the effect of acceleration.
3. The formula  $R = av^2 + bv$  is shown to be a useful approximation to the

\* Pannell, 'Adv. Otec. for Aeronautics Rep. and M.,' No. 190 (1916).

resistance acceleration law; and a more exact expression is found for the resistance during the first few seconds of fall.

4. A critical analysis is made of previous results, including Sir Isaac Newton's.
5. An experiment is recorded in which a roughening of the surface reduced the resistance to motion.

The purchase of the wood chronograph for these experiments was made possible by a grant from the Armstrong College Research Committee. My thanks are also due to the Managers of the Blucher, Usworth, Hebburn, Wearmouth and Silksworth coal-mines for their courteous help.

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### *The Secondary Spectrum of Hydrogen at Higher Pressures.—II.*

By IAN SANDEMAN, M.A., B.Sc., Carnegie Research Scholar, The University, St. Andrews.

(Communicated by Prof. O. W. Richardson, F.R.S.—Received November 5, 1925.)

In a recent paper the author\* has discussed the possibilities presented by the arc spectrum of hydrogen at higher pressures of detecting regularities in the secondary spectrum. In the present paper the same method has been used to investigate further regularities. Four bands are given whose null lines approximately follow a Rydberg law. Of these the most intense band contains a series that has already been given by Richardson and Tanaka.

*P, Q, and R Combination including Richardson and Tanaka's 83 Q.*—With the aid of the arc spectrum an attempt has been made to fit a P and an R series into a combination along with Richardson and Tanaka's 83 Q.† The results recorded in Table I are sufficient to indicate a considerable degree of probability for the proposed combination, more particularly in view of the accuracy with which the Combination Principle holds. The strong Fulcher line 16060·31 is unlikely to be a member of the band, but has been included since it probably overshadows a weaker P(2).

Table I shows the intensities of the lines in the arc at atmospheric pressure and at 45 cms. of mercury as determined by the author, as well as the observa-

\* Sandeman, 'Roy. Soc. Proc.,' A, vol. 108, p. 607 (1925).

† Richardson and Tanaka, 'Roy. Soc. Proc.,' A, vol. 107, p. 618 (1925).

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Table I.—Band IV<sub>A</sub>, 7.

P (m).

m.	Properties.							W. L. in Air.	Wave No.	Intensity.			1st Diff.	2nd Diff.	Low Tem.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)			Atm. Press.	45 cms.	M. & B.			
2	.....	++	=	.....	.....	F	.....	[6224.81	16060.31]	5	5	9	.....	.....	++
3	.....	+	.....	.....	.....	.....	.....	6262.49	15963.68	6	6	4	.....	.....	—
4	+	.....	+	.....	.....	.....	.....	6277.11	15926.51	4	3	3	.....	.....	.....
5	.....	.....	.....	.....	.....	.....	.....	6270.53	15943.22	1	1	1	.....	.....	.....
6	.....	.....	.....	.....	.....	.....	.....	6243.14	16013.17	1	1	—	.....	.....	.....
													Mean Δ = 53.56		

Q (m) (Richardson and Tanaka's 83 Q).

1	++	.....	++	.....	Z	.....	.....	6090.92	16413.35	5	4	7	.....	.....	.....
2	++	.....	.....	.....	Z	.....	.....	6070.00	16469.90	6	5	7	.....	.....	.....
3	++	.....	.....	.....	Z	.....	.....	6027.98	16584.74	7	4	8	.....	.....	+
4	++	.....	++	.....	.....	.....	.....	5967.31	16753.34	7	5	6	.....	.....	.....
5	+	.....	++	O	.....	.....	.....	5889.04	16976.00	9	5	3	.....	.....	.....
6	.....	.....	++	++	.....	.....	.....	5794.65	17252.53	5	4	4	.....	.....	.....
7	.....	.....	.....	.....	.....	.....	.....	5685.97	17582.29	—	—	r	.....	.....	.....
8	.....	.....	++	.....	F	.....	.....	5564.53	17966.00	1	0	2	.....	.....	—
9	.....	.....	.....	.....	.....	.....	.....	5432.40	18402.95	—	—	q	.....	.....	.....
													Mean Δ = 53.64.		

R (m).

1	.....	.....	++	.....	.....	.....	.....	5942.95	16822.02	—	—	1	.....	.....	.....
2	++	.....	++	++	.....	.....	.....	5849.31	17091.30	1	1	6	.....	.....	.....
3	.....	.....	+	.....	.....	.....	.....	5741.80	*17411.32	5	2	2	.....	.....	.....
4	.....	.....	+	+	.....	.....	.....	5620.90	17785.81	4	3	2	.....	.....	.....
5	.....	.....	.....	++	.....	.....	.....	5488.48	18214.95	—	—	†	.....	.....	.....
													Mean Δ = 54.56		

\* The same line as Richardson and Tanaka's 201 R(6). The intensity of this line was very variable on the author's plates. In a previous paper its intensity was given as 2 at atmospheric pressure; more recent plates would, however, indicate a higher figure.

† Recorded by Merton and Barratt as appearing on their helium plates.

tions of Merton and Barratt. The properties of the lines are those given in Merton and Barratt's tables and are in the same order, namely: (1) high pressure, (2) low pressure, (3) condensed discharge, (4) helium effect, (5) Zeeman effect, (6) Fulcher lines, (7) Stark effect. The last column gives the behaviour of the lines at very low temperatures according to the observations of McLennan and Shrum.\* The line 16013·17 is not given by Merton and Barratt; the wave number was determined by striking a mean of the readings from four of the author's plates.

The Combination Principle applied to this band gives:—

			Differences.
Q (1) + Q (2) = 32883·25	R (1) + P (2) = [32882·33]	${}_1\Delta_2 = [-0\cdot92]$	
Q (2) + Q (3) = 33054·64	R (2) + P (3) = 33054·98	${}_2\Delta_3 = +0\cdot34$	
Q (3) + Q (4) = 33338·08	R (3) + P (4) = 33337·83	${}_3\Delta_4 = -0\cdot25$	
Q (4) + Q (5) = 33729·34	R (4) + P (5) = 33729·03	${}_4\Delta_5 = -0\cdot31$	
Q (5) + Q (6) = 34228·53	R (5) + P (6) = 34228·12	${}_5\Delta_6 = -0\cdot41$	

With the exception of the first which involves the strong Fulcher line mentioned above, the differences are within the limits of error. Moreover, if the line Q (5) which appears to be too intense in the arc at atmospheric pressure is excepted, the intensity distribution of the series is also reasonable.

*A Band System.*—In a recent article on the 'General Nature of Band Spectra' Nicholson† remarks that, if the null lines of a band system are given by a Rydberg law, "an ordinary Zeeman effect should only be expected when the constant is N itself." The presence of three strong Zeeman lines in the Q series suggested the desirability of searching the secondary spectrum of hydrogen for other similar bands fitting along with the above into a Rydberg formula. The result of this search is shown in Tables II, III, and IV which indicate the presence of three other bands whose null lines are related by a Rydberg law. If the interpretation given to these lines is correct, the band given above corresponds to the quantum integer 7 in the Rydberg formula and the other three bands to the integers 6, 8, and 9. Certain lines are also given which may belong to the band given by the integer 10; this band, however, is so weak, if it occurs, that its lines cannot at present be stated with certainty. Bands corresponding to integers less than 6 cannot be identified until the measurement of the secondary spectrum has been carried much further into the infra-red. It is hoped to pursue these investigations further in this direction.

\* McLennan and Shrum, 'Trans. Roy. Soc. Canada,' vol. 18, p. 177 (1924).

† Nicholson, 'Phil. Mag.,' No. 297, p. 650 (1925).

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Table II.—Band IV<sub>A</sub>, 6.

P (m).

m.	Properties.							W. L. in Air.	Wave No.	Intensity.			1st Diff.	2nd Diff.	Low Tem.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)			Atm. Press.	45 cms.	M. & B.			
2								6538.46	15289.91	1	1	—			
3								6580.63	15191.94	2	3	—			
4			(calculated)					—	(15154.90)	—	—	—			
5								6589.01	15172.60	2	1	—			

Q (m).

1								6387.87	15650.36	1	2	1			
2								6364.64	15707.46	6	7	2			
3								6318.65	15821.80	3	3	1			
4								6251.66	15991.33	0	0	—			

R (m).

1	+							6221.73	16068.26	8	7	4			
2			++	O				6119.00	16338.03	9	8	3			
3								6001.38	*16658.23	0	—	p			
4	++		++					5869.18	†17033.45	7	5	4			
5				O				5724.55	*17463.80	—	—	q			
6			+	++				5569.51	17949.94	2	1	0			
7				++				5407.03	18491.16	—	—	§			

\* Tanaka's measurements ('Roy. Soc. Proc.,' A, vol. 108, p. 592 (1925)).  
† Recorded by Merton and Barratt as an unresolved doublet—the same line as Richardson and Tanaka's 1P (3).  
§ Measured by Merton and Barratt on their helium plates.

*Combination Principle.*

				Differences.
$Q(1) + Q(2) = 31357.82$	$R(1) + P(2) = 31358.17$	${}_1\Delta_2 = +0.35$		
$Q(2) + Q(3) = 31529.26$	$R(2) + P(3) = 31529.97$	${}_2\Delta_3 = +0.71$		


The wave numbers of the lines recorded for the P series are from preliminary measurements by the author. Although no high degree of accuracy is claimed for these measurements, the Combination Principle holds with moderate accuracy for the lines of lowest quantum number. P(4) was not observed, and the value obtained from the Combination Principle is inserted.

Table III.—Band IV<sub>A</sub>, 8.

P (m).

m.	Properties.							W. L. in Air.	Wave No.	Intensity.			1st Diff.	2nd Diff.	Low Tem.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)			Atm. Press.	45 cms.	M. & B.			
2								6030.39	16561.61	0	1	—			
3		+						6071.62	16465.51	1	1	2	96.10	59.36	
4			++	++				6085.20	16428.77	6	7	0	36.74	53.75	+0.73
5			+					6078.91	16445.78	1	1	3	17.01	52.65	-0.37
6	+		++					6053.27	16515.44	0	0	4	69.66	52.65	-0.37
7								6008.77	16637.75	—	—	0	122.31		
															Mean Δ = 53.02

Q (m).

1			+					5911.73	16910.86	1	0	2		$\delta$	$\delta - \Delta$	
2			++					5891.31	†16909.45	1	0	1		58.59	56.37	
3			+	0				5851.67	17084.41	1	1	3		114.96	53.16	-0.40
4			++	++				5794.65	*17252.53	5	4	4		168.12	53.75	+0.19
5			(missing)					—	[17474.40]	—	—	—		221.87	53.76	+0.20
6			+					5632.23	17750.03	1	—	0		275.63		
Mean $\Delta = 53.56$ .																

\* The same line as IV<sub>A</sub>, 7 Q(9), and IV<sub>A</sub>, 9 Q(1).† The same line as IV<sub>A</sub>, 9 P(7).

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Table III—*continued.*

R (m).

m.	Properties.							W. L. in Air.	Wave No.	Intensity.			1st Diff.	2nd Diff.	Low Tem.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)			Atm. Press.	45 cms.	M. & B.			
1				+	+			5772.50	17318.72	3	0	0			
2			+	+	+			5684.09	17588.10	5	4	4	269.38	50.69	
3			(calculated)					—	(*17908.17)	—	—	—	320.07	52.91	
4			(calculated)					—	(18281.15)	—	—	—	372.98		

\* Tanaka gives a faint line [17909.9].

## *Combination Principle.*

Differences.

$$\begin{array}{llll}
 Q(1) + Q(2) = 33880.31 & R(1) + P(2) = 33880.32 & {}_1\Delta_2 = +0.02 \\
 Q(2) + Q(3) = 34053.86 & R(2) + P(3) = 34053.61 & {}_2\Delta_3 = -0.25
 \end{array}$$

Band IVA, 8 fits into the general scheme for the system. R (3) and R (4) appear, however, to be absent, although Tanaka gives a faint line which nearly coincides with R (3); the values of R (3) and R (4) are inserted from the Combination Principle and give a reasonable second difference. P (4) is abnormally intense in the arc, and may be an overlap from another system. Indeed, this may well be the explanation of the slight irregularity in the second differences of the P series. The line P (4) is missing in Bands IVA, 6 and 9, and it seems strange that it should come out so strongly in the case of this band. In the preceding tables values of missing lines calculated from the Combination Principle have been placed in round brackets. Values in square brackets have been inserted to show that such values are obtainable so as to obey the Combination Principle and at the same time give reasonable second differences.

The series IVA, 6 R, and IVA, 9 P and R give some indication of an alternating series of intensities, a possibility which has been referred to by R. Mecke\* in connection with the helium bands and second positive and negative groups of nitrogen bands. It is noteworthy that the lines P (4), R (3), and R (5) are weak in both the bands mentioned above.

\* Mecke, 'Phys. Zeits.', vol. 26, p. 217 (1925), and 'Zeits. für Physik,' vol. 28, p. 261 (1924).



Table IV.—Band IV<sub>A</sub>, 9.

P (m).

m.	Properties.							W. L. in Air	Wave No.	Intensity.			1st Diff.	2nd Diff.	Low Tem.	
	(1)	(2)	(3)	(4)	(5)	(6)	(7)			Atm. Press.	45 cms.	M. & B.				
2			(calculated)					—	(16903.45)	—	—	—	—	8	8—Δ	
3								5947.96	16807.85	—	—	0	—95.60	57.47		
4			(missing)					—	[16769.72]	—	—	—	—38.13	52.37	+0.02	
5			+	0				5956.42	16783.96	2	1	3	14.24	52.14	—0.21	—
6			(missing)					—	[16850.34]	—	—	—	66.38	52.73	+0.38	
7			++					5891.31	†16909.45	1	0	1	119.11	52.17	—0.18	
8			(missing)					—	[17140.73]	—	—	—	171.28	52.36	+0.01	
9	+		++					5757.33	17364.37	*	*	3	223.64			
															Mean Δ = 52.35.	

\* Not separable on the author's plates from 17366.75 (Intensity: Atm. Press. 6, 45 cms. 3, M. &amp; B. 0).

† The same line as IV<sub>A</sub>, 8 Q (2).

Q (m).

1			++	++				5794.65	*17252.53	5	4	4	58.75	8	8—Δ	
2		++	++					5774.98	†17311.28	4	3	7	114.97	56.22		+
3			+					5736.88	‡17426.25	5	3	8	166.77	51.80	—0.48	++
4			++	++				5682.50	17593.02	7	4	2	219.33	52.56	+0.28	
5		+						5612.53	17812.35	8	3	4	271.72	52.39	+0.11	
6			(missing)					—	[18084.07]	—	—	—	324.10	52.38	+0.10	
7			+					5430.86	18408.17	3	3	0				
Mean Δ = 52.28.																

\* The same line as IV<sub>A</sub>, 7 Q (6), and IV<sub>A</sub>, 8 Q (4).

† Recorded by Merton and Bartlett as an unresolved doublet.

‡ The same line as Richardson and Tanaka's 201 R (2), which is, however, too intense for its position in that series.

Table IV—continued.

R (m).

m.	Properties.							W. L. in Air.	Wave No.	Intensity.			1st Diff.	2nd Diff.	Low Tem
	(1)	(2)	(3)	(4)	(5)	(6)	(7)			Atm. Press.	45 ema.	M. & B.			
1								5660.83	17660.36	3	1	0	269.07	8	8-Δ
2								5575.88	17029.43	1	—	—	320.12	51.05	
3			(missing)					—	[18249.55]	—	—	—	372.52	52.40	+0.42
4								5368.48	*18622.07	0d	0d	qd	424.01	51.49	-0.49
5			(missing)					—	[19046.08]	—	—	—	476.06	52.05	+0.07
6								5120.97	19522.14	0	—	1			
Mean Δ = 51.98.															

\* Tanaka's measurement.

d signifies diffuse.

## Combination Principle.

Differences.

$$Q(2) + Q(3) = 34737.53 \quad R(2) + P(3) = 34737.28 \quad {}_2\Delta_3 = -0.25$$

$$Q(4) + Q(5) = 35405.37 \quad R(4) + P(5) = 35406.03 \quad {}_4\Delta_5 = +0.66$$

$$Q(6) + Q(7) = [36492.24] \quad R(6) + P(7) = 36491.59 \quad {}_6\Delta_7 = -0.65$$

Apart from this alternation the intensity sequence of all the series is extremely regular. The following lines are not given by Merton and Barratt or by Tanaka, but were measured from the plates of the arc spectrum:—IV<sub>A</sub>, 6 P (2), P (3), P (5), and Q (4), IV<sub>A</sub>, 7 P (6), IV<sub>A</sub>, 8 P (2), and IV<sub>A</sub>, 9 R (2). A curious feature of the bands is that IV<sub>A</sub>, 9 Q, is a more intense series than IV<sub>A</sub>, 8 Q, suggesting that intensity may alternate with the electron quantum number as well as with the rotation quantum number.

The term differences for all four bands are shown in Tables V and VI. Term differences for the next fragmentary Band IV<sub>A</sub>, 10 have also been added for comparison. The notation adopted is that of Richardson and Tanaka, viz.:—

$$\left. \begin{aligned} P(m) &= v_0 + F(m-1) - f(m) & m-1 &\rightarrow m \\ Q(m) &= v_0 + F(m) - f(m) & m &\rightarrow m \\ R(m) &= v_0 + F(m+1) - f(m) & m+1 &\rightarrow m \end{aligned} \right\} \quad (1)$$

Whence

$$\left. \begin{aligned} F(m+1) - F(m) &= R(m) - Q(m) & &= Q(m+1) - P(m+1) \\ (m+1) - f(m) &= R(m) - Q(m+1) & &= Q(m) - P(m+1) \end{aligned} \right\} \quad (2)$$

The term differences  $F(m+1) - F(m)$  were got by taking the average of the pair of quantities  $R(m) - Q(m)$  and  $Q(m+1) - P(m+1)$ ; when, however, one of the pair seemed more reliable than the other, it alone was used. A similar procedure was adopted for the final term differences  $f(m+1) - f(m)$ .

The secondary spectrum of hydrogen contains such a mass of lines, that it is quite possible that stronger lines belonging to other systems have been included in the preceding tables, when they overshadow weak members of the system—indeed the strong line IVA, 8 P(4) may be an example of this. Yet the general coherency of the fourth columns of Tables V and VI is sufficiently striking, and indicates that the majority of the lines have been correctly identified. In view of the above consideration and the difficulty of measuring very weak lines accurately, the figures referring to the higher quantum numbers may not be entirely trustworthy; all the calculable term differences have, however, been given, and where the reckoning of these has involved calculated lines, this fact has been indicated by placing the term difference in brackets.

Two important conclusions arise from a consideration of Tables V and VI: the first is that the final terms are not the same for all the bands, although we should have expected them to be the same from the fact that the null lines appear to follow a Rydberg law. Moreover, the fact that the final terms are not the same, seems to clash with the results obtained for the doublet bands of helium by Curtis and Long\* who found the final terms to be constant throughout each series of doublet bands. Indeed, Curtis and Long say that “the arrangement of the bands in a Rydberg series is conclusive evidence for a common final term for them all.” We must bear in mind, however, that hydrogen is an exceptional element, and that the bands under consideration differ from the normal band types in at least one other respect, viz., the very large displacement of the lines corresponding to the lowest quantum integers from the position indicated by a parabolic series-law. Reasons will be given for thinking that the final terms should not be exactly the same when the question of representation of the bands by a formula is discussed.

The second conclusion which arises from a consideration of Tables V and VI is that none of the bands can be represented by the formula of Kramers and Pauli.† Their formula may be written

$$F(m) = B(\sqrt{m^2 - \sigma^2} \mp \rho)^2, \quad (3)$$

B being equal to  $h/8\pi^2 I$ , where I is the moment of inertia of the molecule, and

\* Curtis and Long, ‘*Roy. Soc. Proc., A*, vol. 108, p. 513 (1925).

† Kramers and Pauli, ‘*Zeits. für Physik*,’ vol. 13, p. 351 (1923).

Table V.—Initial Term Differences.

Band IV <sub>A</sub> .	<i>m</i> .	$F(m+1) - F(m)$ .	$\Delta \{F(m+1) - F(m)\}$ .	$\Delta^2 \{F(m+1) - F(m)\}$ .
6	1	417.90	212.67	— 0.81
	2	630.57	205.86	— 0.17
	3	836.43	205.69	
	4	1042.12		
7	1	408.67	212.56	— 7.085
	2	621.23	205.475	+ 0.445
	3	826.705	205.92	+ 0.61
	4	1032.625	206.53	
	5	1239.155		
8	1	407.855	210.92	— 5.935
	2	618.775	204.985	— 0.125
	3	823.76	204.86	+ 1.11
	4	(1028.62)	205.97	
	5	1234.59		
9	1	407.83	210.57	— 5.67
	2	618.40	204.90	+ 0.52
	3	(823.30)	205.42	— 0.41
	4	1028.72	205.01	— 0.345
	5	(1233.73)	204.665	
	6	(1438.395)		
10	1	408.05	210.33	
	2	618.38		

$\sigma h/2\pi$  and  $\rho h/2\pi$  being components of the resultant electronic angular momentum along the line of the nuclei, and in a direction at right angles to it in the plane given by the line of the nuclei and the direction of the resultant electronic angular momentum. The author\* has already shown that, when a series can

\* Sandeman, *loc. cit.*

be represented by the formula (3), the quantities  $\Delta^2 \{F(m+1) - F(m)\}$  are all of the same sign and tend steadily to zero with increasing rotation quantum number. All the observed quantities  $\Delta^2 \{F(m+1) - F(m)\}$  and

Table VI.—Final Term Differences.

Band IVa.	<i>m</i> .	$f(m+1) - f(m)$ .	$\Delta \{f(m+1) - f(m)\}$ .	$\Delta^2 \{f(m+1) - f(m)\}$ .
6	1	360.80	155.43	- 4.76
	2	516.23	150.67	+ 1.16
	3	666.90	151.83	
	4	818.73		
7	1	352.12	154.27	- 2.555
	2	506.39	151.715	+ 0.145
	3	658.105	151.86	+ 0.80
	4	809.965	152.66	
	5	962.625		
8	1	340.265	154.55	- 2.725
	2	503.815	151.825	- 0.715
	3	655.64	151.11	+ 1.10
	4	806.75	152.21	+ 1.11
	5	(958.96)	153.32	
	6	1112.28		
9	1	349.08	154.35	- 1.25
	2	503.43	153.10	- 0.24
	3	(656.53)	152.86	- 0.24
	4	809.39	152.62	- 0.335
	5	(962.01)	152.285	+ 0.86
	6	(1114.295)	153.145	
	7	(1267.44)		
10	1	349.10		

$\Delta^2 \{f(m+1) - f(m)\}$ , with the exception of those obtained from the faint Band IV<sub>A</sub>, 9, increase with rise of the quantum number  $m$  and pass from negative to positive. They therefore show considerable regularity, but not the particular type of regularity demanded by the formula of Kramers and Pauli.

In the absence of a suitable theoretical formula, since the bands obey a parabolic law closely, the following formula has been employed :—

$$\left. \begin{aligned} F(m) &= B(m + \Lambda)^2 \\ f(m) &= b(m + \lambda)^2 \end{aligned} \right\}, \quad (4)$$

where  $\Lambda$  and  $\lambda$  are constant for each band. Here  $m + \Lambda$  represents the "effective" initial quantum number. If the general significance of the method of Kramers and Pauli is admitted the constants  $\Lambda$  and  $\lambda$  must be understood as determined by the mutual orientation of the intra-molecular axes. Table VII shows the calculated values of the constants for each band and clearly indicates a diminution of  $\lambda$  with rise in electron quantum number. Thus, on account of the different mutual orientation of the intra-molecular axes, the final terms may not be the same, although the electron energy may be determined by the same quantum number. A theoretical treatment of this question, which is intimately bound up with the peculiar displacement from the parabolic law of the lines corresponding to the lowest quantum integers, is reserved for a future paper.

In the compilation of Table VII, since the higher members of the bands are weak and not entirely trustworthy, and since the object of the table is to facilitate a comparison between the bands, an approximate procedure has been adopted: to determine  $B$  and  $b$  we have the relations

$$\left. \begin{aligned} 2B &= \Delta \{F(m+1) - F(m)\} \\ 2b &= \Delta \{f(m+1) - f(m)\} \end{aligned} \right\}. \quad (5)$$

Actually  $B$  and  $b$  were calculated from the quantities  $\Delta \{F(3) - F(2)\}$  and  $\Delta \{f(3) - f(2)\}$  taken from Tables V and VI. This means that the observed values of the lines P (3), P (4), Q (2), Q (3), Q (4), R (2), and R (3) were alone used in determining these constants.  $\Lambda$  and  $\lambda$  were then determined from the relations

$$\left. \begin{aligned} B(2m+1+2\Lambda) &= F(m+1) - F(m) \\ b(2m+1+2\lambda) &= f(m+1) - f(m) \end{aligned} \right\}, \quad (6)$$

which follow from equations (4), the data used being the same as before. The values of the initial and final moments of inertia corresponding to  $B$  and  $b$  are also shown in Table VII. The regularity with which the constants vary from band to band in Table VII is very striking.

Table VII.—Constants of the Bands.

Band IV <sub>A</sub> .	$B$ .	$I_1$ gm. (cms.) <sup>2</sup> .	$\Lambda$ .	$b$ .	$I_2$ gm. (cms.) <sup>2</sup> .	$\lambda$ .	$\nu_0$ (from Table VIII).
6	102.93	$2.685 \times 10^{-41}$	0.503	75.34	$3.669 \times 10^{-41}$	0.926	15676.49
7	102.74	$2.690 \times 10^{-41}$	0.523	75.86	$3.644 \times 10^{-41}$	0.838	16428.34
8	102.49	$2.697 \times 10^{-41}$	0.519	75.91	$3.641 \times 10^{-41}$	0.818	16921.88
9	102.45	$2.698 \times 10^{-41}$	0.518	76.55	$3.611 \times 10^{-41}$	0.788	17258.76

The method of obtaining the null lines,  $\nu_0$ , is illustrated in Table VIII. If the parabolic formula representing any series is

$$\nu = \alpha + \beta m + \gamma m^2,$$

then we have for a P series

$$\nu_{0P} = \alpha_P - (1 - \Lambda)^2 B + \lambda^2 b,$$

for a Q series

$$\nu_{0Q} = \alpha_Q - \Lambda^2 B + \lambda^2 b,$$

and for a R series

$$\nu_{0R} = \alpha_R - (1 + \Lambda)^2 B + \lambda^2 b.$$

The mean of the three values was taken as the null line for each band. In all the Bands except IV<sub>A</sub>, 6, the values of the constants  $\alpha$ ,  $\beta$ ,  $\gamma$ , were found to differ considerably with the number of lines used in reckoning them. Consequently the lines given by the quantum integers 2, 3, 4 and 5 alone were used, as these seemed the most trustworthy. Table VIII shows the lines which were used in each case. For the sake of consistency the same procedure was followed in the case of Band IV<sub>A</sub>, 9, the calculated values of missing lines being employed. This method of determining the constants, although admittedly approximate, was the only one that seemed to promise a fair comparison between the various bands.

Table VIII.—Calculation of  $\nu_0$ .

Band IVa.	Series.	$\nu_0$ .	Lines used.	Mean $\nu_0$ .
6	P	15676.48	All lines except P (2)	15676.49
	Q	15676.34	All lines except Q (1)	
	R	15676.64	All lines except R (1)	
7	P	16428.37	P (3), P (4), P (5)	16428.34
	Q	16427.15	Q (2), Q (3), Q (4), Q (5)	
	R	16429.49	R (2), R (3), R (4)	
8	P	16921.48	P (3), P (4), P (5), P (6)	16921.88
	Q	16922.28	Q (2), Q (3), Q (4)	
	R	—	—	
9	P	17260.23	P (3), P (4), P (5)	17258.76
	Q	17258.20	Q (2), Q (3), Q (4), Q (5)	
	R	17257.86	R (2), R (3), R (4)	

The successive values of  $\nu_0$  may be represented by the Rydberg formula

$$18567.47 - \frac{109678.3}{(n + 0.159883)^2}$$

with residuals\*  $-0.46, +0.35, +1.64, -1.51$ ,  $n$  taking the values 6 to 9. In view of the approximate method used to determine the values of  $\nu_0$ , the formula appears to fit very well. It is of special interest to find that the null lines can be arranged in this way. Although in the case of helium Fowler and others have shown that the "heads" satisfied a formula of the Rydberg type, this appears to be the first time such a result has been shown to hold for hydrogen.

*The Band corresponding to  $n = 10$ .*—Since, apart from the Q series, Band IVa, 9 is very faint both in the arc and in the Geissler tube determinations of Merton and Barratt, it is not to be expected that lines belonging to Band IVa, 10 can be identified with certainty. The following lines are probably the first two members of the Q and R series (Table IX).

\* With these values we may compare the residuals given by Curtis and Long for the second series of the doublet bands of helium, viz., 0,  $+2.0$ ,  $+2.1$ , 0.



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Table IX.—Band IV<sub>A</sub>, 10.

Q (m).

m.	Properties.							W. L. in Air.	Wave No.	Intensity.			1st Diff.	Low Tem.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)			Atm. Press.	45 cms.	M. & B.		
1	.....	++	++	.....	.....	.....	.....	5713·30	17498·18	5	2	4	> 58·95	
2	.....	.....	.....	.....	.....	.....	.....	5694·11	17557·13	3	0	2		

R (m).

1	.....	.....	.....	.....	.....	.....	.....	5583·10	17906·23	—	—	0	> 269·28	
2	.....	.....	.....	.....	.....	.....	.....	5500·39	18175·51	—	—	0		

No line corresponding to Q (3) is given in the Tables of Merton and Barratt or in those of Tanaka, and the arc spectrum in this region shows such a mass of faint overlapping lines that all attempts at measurement of these with the dispersion available had to be abandoned. The line 18494·96 (2, 1, 0) may be R (3), but this appears unlikely since its intensity is too great, while R (3) is missing in Bands IV<sub>A</sub>, 8 and 9. No lines could be detected corresponding to P (2) or P (3), and indeed P (2) is missing in Band IV<sub>A</sub>, 9. The term differences deducible from the four lines given are entered in Tables V and VI. They are in close agreement with those of the other bands.

In order to test the correctness of the allocation of the above four lines to this band, the constants B, *b*,  $\Lambda$ , and  $\lambda$  for Band IV<sub>A</sub>, 10 were estimated by plotting the values for the other four bands given in Table VII, and drawing a smooth curve as nearly as possible through the four points obtained. On extrapolating these curves the values  $B = 102\cdot32$ ,  $b = 77\cdot28$ ,  $\Lambda = 0\cdot511$ ,  $\lambda = 0\cdot769$  were obtained. From the Rydberg formula the value of  $\nu_0$  for this band should be 17504·93, and on calculating Q (2) from these data the value 17557·54 was obtained which comes very near the wave number given.

*Other Regularities.*—Another set of bands closely resembling those given has been detected whose null lines appear to be given by a Rydberg formula in which *n* takes the same values. These are at present being arranged.

*Summary.*

The arc spectrum of hydrogen at higher pressures has been employed to detect further regularities in the secondary spectrum.

With its aid a P and an R series have been selected fitting along with Richardson and Tanaka's 83 Q into a P, Q, and R Combination, and closely conforming with the Combination Principle.

This band is one of four bands whose null lines are given by the Rydberg formula

$$18567 \cdot 47 - \frac{109678 \cdot 3}{(n + 0 \cdot 159883)^2}$$

where  $n$  takes the values 6, 7, 8, and 9. Indications have also been obtained of a band corresponding to the integer 10.

I wish to express my obligation to the Department of Scientific and Industrial Research for assistance in the purchase of apparatus, and, as in the work described in the previous paper, my grateful thanks to Prof. H. Stanley Allen for his interest and guidance.

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*The Mobility of Ions in Air.—Part I. Negative Ions  
in Moist Air.*

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*Introduction.*

The mobility of "small" ions at atmospheric pressure and temperature has been the subject of investigation at intervals for more than a quarter of a century, and one would have imagined that unanimity of opinion on the numerical values would have been reached in the case of the commoner gases. And yet this is by no means the case.

In the case of negative ions in air, with which the present paper is concerned, there is wide disagreement between the values obtained for the mobility by different observers, and it is disputed whether the ions are all of the same mobility or are distributed in groups of several different mobilities.

*The differences between the numerical values obtained by different observers are rather surprising. Most of the more recent work has been carried out with some modification of the original alternating field method of Rutherford, the appropriate sign of ions being introduced through a gauze into the main chamber by an auxiliary field. In some cases there is definite evidence that the results obtained depend upon the value of the auxiliary field. Loeb\* has examined this effect and has shown that it is due to interpenetration of the two fields on opposite sides of the gauze. When he eliminated the effect by making the fields equal he obtained the value 2.20 for the mobility of the negative ion in dry air. This is considerably higher than the mean of the earlier values, 1.80 (Kaye and Laby's tables), but is in agreement with a previous value of his, 2.18, obtained without a gauze by generating the ions directly in the chamber by ultra-violet light.† An examination of the earlier experimental work does not make the cause of the discrepancy quite clear, several of the earlier observers (e.g., Zeleny‡) having made careful tests and allowances for possible errors.*

The view that the ions consist of a mixture of groups of different mobilities has been put forward by Nolan, who claims that the curves obtained by the alternating field method show a number of "breaks" or "kinks," each of which corresponds to a distinct group. Loeb, however, does not consider that the accuracy of the experimental points justifies this treatment.

All observers agree that the effect of water vapour is to reduce the average mobility of the ions; Zeleny, for instance, obtained the values 1.87 in dry air and 1.51 in saturated air. No detailed observations of the variation of mobility with humidity appear, however, to have been made.

It was felt that further experimental work on all these questions was desirable. The present paper describes a series of experiments made by a new method which was designed to measure absolute values of mobility to a high degree of accuracy, and to give a separate "peak" in the curve obtained for each group of ions present. The present form of the method has, however, the disadvantage that it cannot be used for *extremely* dry air.

#### *Principle of the Method.*

An alternating field of the "square-wave" type is applied between two parallel metal plates, A and B (fig. 1), A being connected to an electrometer

\* Loeb, 'Journ. Franklin Inst.,' vol. 196, p. 771 (1923).

† Loeb, 'Journ. Franklin Inst.,' vol. 196, p. 537 (1923).

‡ Zeleny, 'Phil. Trans., A,' vol. 195, p. 193 (1900).

and kept approximately at earth potential, while B is connected to the source of alternating potential applied through a commutator, C. Calling the phase of the alternating field during which B is negative the "advancing phase" (since we are dealing with negative ions) and the other the "retreating phase"; it is arranged that the retreating phase lasts considerably longer than the advancing phase.

Towards the end of the retreating phase in each cycle a flash of ionisation occurs near B, say, in the dotted area in fig. 1. (In practice, the flash is produced by  $\alpha$  rays from a strip of polonium placed on a rotating wheel on the same shaft as the commutator; it is thus kept synchronised with the alter-

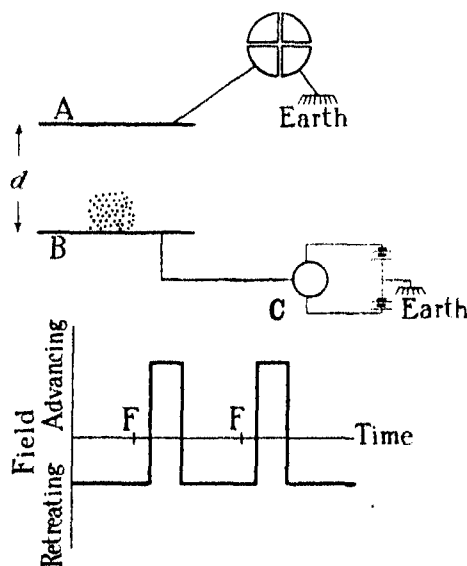


FIG. 1.

nating field.) The times for which the advancing phase and the retreating phase last, and the time which elapses between the end of the flash of ionisation and the commencement of the advancing phase, are all inversely proportional to rate of rotation of the commutator, and we may call them respectively  $\alpha/N$ ,  $\beta/N$  and  $\gamma/N$  where  $N$  is the frequency of rotation and  $\alpha$ ,  $\beta$  and  $\gamma$  are certain angles on the commutator.

When the flash occurs, the negative ions generated move down in the reversing field towards B. At a time  $\gamma/N$  later the advancing phase begins. In that time some or all of the ions have reached B, the number which have done so depending on  $N$ . Those that remain move in the advancing field towards A

for a time  $\alpha/N$ . Any of these which do not strike A in this time are then in the reversing field again, and it is arranged that the reversing phase lasts long enough to remove them all to B (*i.e.*, that  $\alpha/N$  is always big enough for this to occur).

Omitting for the moment any consideration of the positive ions formed in the flash, let us consider the effect on the current arriving at A of increasing the frequency of the commutator from a low value. At very low frequencies the time  $\gamma/N$  is sufficient to collect all the ions at B, and none will reach A. As the frequency increases the time will come when some of the ions miss B and travel towards A in the advancing field. The flash of ionisation is so timed (*i.e.*,  $\gamma$  is so chosen) that when this occurs  $\alpha/N$  is long enough for them to reach A. With further increase of frequency the number missing B and striking A increases, and the curve showing rate of deflection of electrometer plotted with frequency rises somewhat sharply. But as the frequency is raised there comes a point when some of the ions missing B at the beginning of the advancing phase also miss A at the close of the advancing phase; and this effect increases rapidly with further rise of frequency, so that the rate of deflection curve rapidly falls. In other words, the curve passes through a maximum, the position of which is shown by consideration to be settled by ions which *just* miss B and *just* reach A, and which, therefore, travel the complete distance AB in time  $\alpha/N$ . Their mobility is, therefore, given by  $\kappa = D^2N'/V\alpha$  where D is the distance between the plates, V the advancing voltage, and N' the frequency corresponding to the maximum current.

It will be seen that the conditions necessary for the "peak" to be sharp are that the thickness of the layer of ions which just misses B, and is just caught by A at the maximum, should be small compared with its original distance from either plate, and that diffusion and self-repulsion should be small. The layer can be made thinner by making the flash occur earlier in each cycle (*i.e.*, by increasing  $\gamma$ ; this increases the number of ions caught by B at the frequency of the maximum) but the thinness of the layer which can be used is, of course, limited by the sensitivity of the electrometer and by the intensity of the source of  $\alpha$  rays. Diffusion and self-repulsion can be made small by using high fields.

So far we have neglected any effect which might be produced by ions of the opposite sign to those being dealt with. When the flash of ionisation occurs these ions commence moving towards A in the reversing phase, and if the frequency is lower than a certain value some of them will reach A before the advancing phase occurs; while, if the frequency is higher than another value,

some of them will fail to be drawn back to B in the advancing phase and will strike A in the subsequent reversing phase. It is necessary to ensure that none of these ions reach A at frequencies in the neighbourhood of the peak, and this is done by making all the ionisation occur much closer to B than A.

A somewhat stricter treatment of the theory of the method is as follows :—

Let  $q_x$  be the number of pairs of ions generated per second per layer, 1 cm. thick, at a height  $x$  above the plate B during the flash of ionisation; and let  $\delta/N$  be the duration of the flash. (It is assumed here that the rate of production of ions at any point is constant during the flash. It will be seen later that this assumption is not justified in the apparatus used; but it appears from physical consideration that if  $\delta$  is small the error introduced in this way will be unimportant and will not affect the position of the maximum of the peak.) Let  $h$  be the greatest height above the lower plate to which the ionisation extends, and let  $V'$  be the reversing voltage.

Consider the negative ions. During the flash they move downwards with velocity  $\kappa V'/D$  for time  $\delta/N$ . At the end of the flash the number in a layer  $dx$  thick at height  $x$  above the lower plate is :—

$$\left[ \int_x^{x + \kappa V' \delta / DN} \frac{D}{\kappa V'} q_x dx \right] dx.$$

These ions move downwards with velocity  $\kappa V'/D$  for time  $\gamma/N$ , hence the number left above B at the commencement of the advancing phase is

$$\int_{\kappa V' \gamma / DN}^h \left[ \int_x^{x + \kappa V' \delta / DN} \frac{D}{\kappa V'} q_x dx \right] dx. \quad (1)$$

These move upwards with velocity  $\kappa V/D$  for time  $\alpha/N$ . Thus, if  $\kappa V \alpha / DN > D$  or  $N < \kappa V \alpha / D^2$  they all cross so that the current arriving at the electrometer (in electronic charges per revolution of the commutator) is given by (1).

But if  $\kappa V \alpha / DN < D$  only those ions above  $D - \kappa V \alpha / DN$  cross, and the number reaching the electrometer per revolution is

$$\int_{\frac{\kappa V \gamma}{DN} + (D - \frac{\kappa V \alpha}{DN})}^h \left[ \int_x^{x + \kappa V \delta / DN} \frac{D}{\kappa V} q_x dx \right] dx. \quad (2)$$

The average current is therefore equal to this expression multiplied by  $Ne$ .

When  $N = \kappa V \alpha / D^2$  (2) reduces to (1), but the variation with  $N$  of (1) is different from that of (2), showing that the curve is discontinuous here. If we consider the outer integral we see that the value of its lower limit decreases with  $N$  below this critical value and increases above the critical value (since  $V \alpha > V' \gamma$ ). This suggests that the critical frequency may correspond to the maximum of the

curve, and it can easily be shown that this must be so if  $\delta$  is very small. In practice no discontinuity in the slope of the curve was ever found except at the maximum :

(1) vanishes when  $h = \kappa V' \gamma / DN$  or  $N \equiv \kappa V' \gamma / h D$ ,

(2) vanishes when  $h = (\kappa V' \gamma - \kappa V \alpha) / (DN) + D$

or

$$N \equiv \kappa (V \alpha - V' \gamma) / D (D - h).$$

Hence, the curve strikes the axis at these points. It is clear that by increasing  $\gamma$  the peak can be sharpened; the limiting case is reached when  $\gamma$  is given by  $h/D = V' \gamma / V \alpha$ , since these two frequencies then coincide at the critical frequency  $\kappa V \alpha / D^2$ , and the peak vanishes.

#### *Details of Apparatus.*

The apparatus is shown diagrammatically in fig. 2. "abcd" is a box.

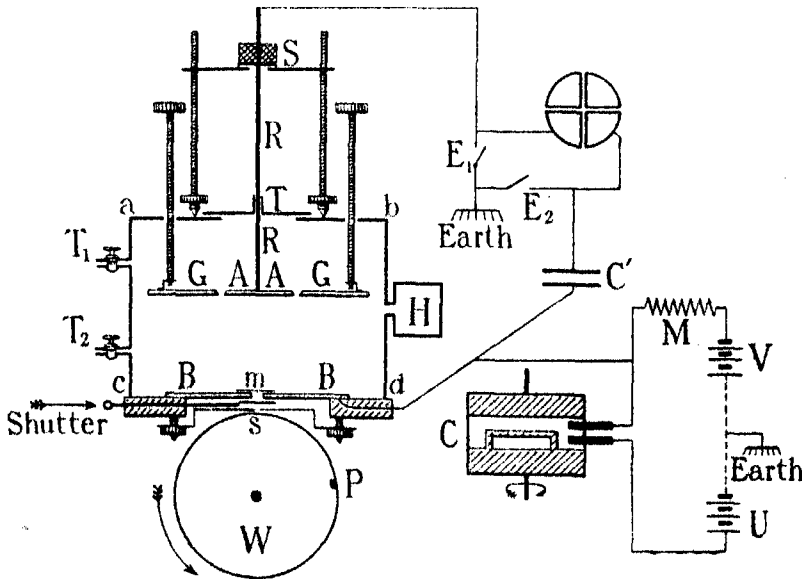


FIG. 2.

7 inches  $\times$  7 inches  $\times$  5 inches, the sides and top of which are  $\frac{1}{4}$  inch brass. The base is of  $\frac{1}{2}$  inch ebonite, with a hole 4 inches square in the middle.

The electrode A is 2 inches square and is made of  $\frac{1}{8}$  inch aluminium. It is supported by a brass rod RR, which is held by a sulphur plug S. This plug is mounted on a table fitted with long levelling screws, so that the electrode A

can be accurately levelled at any desired height above the plate BB. The rod RR enters the box through a brass tube T,  $1\frac{1}{2}$  inches long, which it does not quite touch, the diameter of the rod being  $\frac{5}{32}$  inch and the internal diameter of the tube  $\frac{1}{4}$  inch. The reason for putting the plug S outside the box is that this arrangement prevents water vapour in the box condensing on S at very high humidities; it will be seen later that it is necessary to use extremely good insulation. GG is a guard ring of  $\frac{1}{8}$  inch aluminium supported by long levelling screws, so that it can always be brought accurately into the same plane as A. About  $\frac{1}{32}$  inch clearance is allowed around A, and the edges are bevelled in the manner shown to decrease capacity. The rod RR is connected by a fine wire to one pair of quadrants of a sensitive electrometer E, the whole insulated system being carefully screened.

On the ebonite base of the box is placed an aluminium plate BB, 5 inches  $\times$  5 inches  $\times$   $\frac{1}{8}$  inch, to which an alternating potential can be applied. In the middle of this plate is a hole  $\frac{3}{8}$  inch  $\times$  1 inch, which is covered by a sheet of very thin mica "m" made conducting by laying on it a sheet of very fine aluminium leaf, the leaf completely covering the mica and touching the plate BB all round it. This arrangement forms a window through which  $\alpha$ -rays can enter the box, its stopping power being about a centimetre of air. Flashes of ionisation are produced by a strip of polonium P, 20 mm.  $\times$  5 mm. placed on the circumference of a rotating wheel W of diameter 6 inches. Once in each revolution the strip of polonium passes under a slit S, usually about 3 mm. wide. This slit can be raised or lowered by means of levelling screws; in practice the height of the slit is so adjusted that there is about 2 mm. clearance between it and the rotating wheel. Above the slit (between it and the mica window) is a shutter, and when this is closed none of the  $\alpha$ -rays enter the box.

With such a window, fluctuations of atmospheric pressure would be a source of some danger if some communication with the outside air were not present. This is provided by the opening at T. At the same time, this opening is so restricted that diffusion of water vapour through it can have little effect on the humidity.

The potentials applied to BB are derived from a battery of dry cells VU. The positive pole of the battery U is connected to B through the commutator C (which alternately makes and breaks contact) and the negative pole V is connected to BB through a megohm M, some intermediate point in the battery being earthed. When the commutator makes contact BB takes up the potential of U, and when the circuit through the commutator is broken BB takes up that of V. The commutator is made from an ebonite drum, 4 in.



in diameter on to which a brass band  $1\frac{1}{2}$  in. wide is fitted. Two copper brushes rub on the band, each brush being  $\frac{1}{2}$  in. wide. An insulated brass section is let in to the band in the path of one of the brushes so that when the brush touches this, contact between the two is broken (so as to produce the "advancing phase" of the alternating field). Two lengths of sector were used at different times during the experiments; 4 in. and  $1\frac{1}{2}$  in. It is necessary to ensure that the resistance of the insulation between the insulated sector and the remainder of the brass band is very large compared with a megohm. An air gap about 1 mm. wide is, therefore, left between the ends of the sector and the band, the ebonite being cut away underneath. With a gap of this width the jump of the brush at the passage across is constant and negligible in its effect. The commutator is driven by an electric motor the speed of which can be varied by means of a series resistance. The rate of rotation of the commutator is measured by means of a tachometer, the accuracy of which had been tested by calibration with a stroboscopic disc. The fraction of each revolution for which the advancing field acts (*i.e.*,  $\alpha$  above) is measured by connecting a battery to a standard voltmeter through the commutator and noting the readings when the commutator is stationary (in the "reverse" position) and when it is running. It was shown that the reading with the commutator running was independent of the rate of rotation over the range of frequencies employed.

For measuring the E.M.F. of the cells a voltmeter of very high resistance is necessary, and it was found that none of the electrostatic voltmeters in the laboratory were sufficiently reliable. A standard voltmeter of low range and accurately known resistance was, therefore, used, it being connected in series with a standard megohm and shunted when necessary by means of a resistance box.

Since the "advancing" battery acts through the megohm  $M$ , any leak to earth comparable with a megohm in any part of the system connected to  $B$  will prevent  $B$  from taking up the potential of  $V$  during the advancing phase, and a leak through the commutator will have the same effect. A good deal of trouble was, in fact, experienced from such leaks. To test for leaks the commutator is placed in the "advancing" position and the voltmeter and megohm described above connected between  $B$  and earth. The reading of the voltmeter under these conditions should be very slightly greater than half its reading when connected (with the megohm in series) directly to  $V$ ; the exact theoretical reading being easily calculable. Any leak causes the reading to be lower than this. This test was applied frequently during mobility measurements.

The alternating potential of B acts inductively on the electrometer, so that when the commutator is running the average potential of the pair of quadrants connected to the electrode A is different from that of earth, whether the earthing key E is raised during the advancing or the retreating phase of the field; and this sends the spot of light off the scale. To eliminate this effect both pairs of quadrants are insulated from earth, the pair which is not connected to A being connected to one plate of a variable air condenser C', the other plate of which is connected to B. This condenser is so adjusted that when a potential is applied to B (with both earthing keys  $E_1$  and  $E_2$  raised) no inductive kick of the electrometer is observed. Several other methods of eliminating the effect are possible, but this one has the great advantage that it also eliminates any deflections of the electrometer due to fluctuations in the E.M.F. of the cells. (Under the conditions of the experiment, a fluctuation amounting to only a small fraction of 1 per cent. of the E.M.F. would have produced an easily-measurable deflection of the electrometer by induction.) The insulation of the second pair of quadrants has, however, the disadvantages that it decreases the sensitivity (to charge) of the electrometer and introduces fresh sources of possible leak. In order to ensure that the mobility measurements should not be affected by the inductive action of the field the earthing keys are always raised during the advancing phase--so that the electrode A is always at earth potential (apart from any ionic charges it has received) during this phase of the field. Since the position of the peak is determined solely by the advancing phase of the field the induced charge on A during the reversing phase does not affect the value obtained for the mobility.

*Arrangements for Obtaining Air of Known Humidity.*

In order to obtain air of various humidities solutions of sulphuric acid of known strength were employed; the vapour pressure of each solution being known from Regnault's results. The usual procedure was to place four Petrie dishes (diameter about  $1\frac{1}{2}$  inch) of acid on the guard ring G, and four porcelain boats of the acid on the ebonite insulation round the bottom plate B. The box was then closed and a current of air was blown into it through the tap  $T_1$  (escaping by the tap  $T_2$  and the tube T). This air stream, produced by a rotary blower, was first bubbled through four wash-bottles containing acid of the same strength connected in series and then passed through a glass-wool filter to remove the possibility of drops of acid entering the box. After about half an hour the air current was shut off and the taps  $T_1$  and  $T_2$  closed. Several hours were then allowed to elapse before mobility measurements were made;

in fact in many cases the air stream was passed through in the evening and mobility readings were not made until the following morning.

It was felt that under these conditions the air in the box would almost certainly be accurately in equilibrium with the vessels of acid, but as an additional check the humidity was measured directly by means of a thermal hygrometer\* (shown at H in fig. 2). This hygrometer has the advantage that it does not require the removal of any air from the box. In the instrument used the thermocouple was normally connected to a brass vessel containing phosphorous pentoxide. It could then be exposed either to another brass vessel containing acid of known strength or to the mobility chamber. In order to measure the humidity in the mobility box the galvanometer kick on turning the thermojunction from dry air to the box was compared with the kick on turning from dry air to the second vessel. The sensitivity of the instrument was such that on turning from dry air to saturated air a kick of about 25 cm. was obtained. The agreement between the value of the humidity calculated from the strength of the acid in the mobility box and the value calculated from the hygrometer readings was usually within about 5 per cent. of the amount of water vapour present.

In the case of very wet air (obtained by using pure water instead of acid) the hygrometer readings showed that saturation had not been attained; the humidity being about 90 per cent. The first of the four wash bottles through which the air stream passed was therefore heated to about 40° C. The hot wet air issuing from this bottle was cooled by its passage through the other three vessels (where a great deal of its moisture condensed). In this way humidity in the mobility chamber was increased very nearly to saturation, the value given by the hygrometer being 97 per cent. It should, however, be admitted that the hygrometer is not very accurate at high humidities.

For reasons given above it was impossible to obtain extremely dry air. The greatest degree of drying was obtained by placing phosphorous pentoxide instead of sulphuric acid in the boats and dishes in the mobility box, and passing in a stream of air through the four wash bottles (all containing pure sulphuric acid), and through two tubes containing phosphorous pentoxide (on glass wool) in series with the wash bottles. The hygrometer readings gave values of about 0 to  $\frac{1}{2}$  per cent. for the relative humidity, but the accuracy of the instrument is doubtful in very dry air (as in very wet) and the minute galvanometer kick due to condensation of water vapour round the thermojunction was liable to be masked by irregular movements which were attributed to slight temperature fluctuations.

\* Tyndall and Chattock, 'Proc. Phys. Soc.,' vol. 34, p. 72 (1922).

*Experimental Procedure.*

Air of any required humidity having been introduced into the box, mobility measurements were carried out in the following way, two observers being necessary. With the commutator stationary in such a position that the advancing phase of the field was acting the advancing voltage was measured (it was necessary to carry out this measurement frequently owing to gradual changes in the E.M.F. of the battery which were attributed to temperature variations), and the system connected to the plate B was tested for leaks as described above. With the advancing field still on, the keys  $E_1$  and  $E_2$  were lifted. The commutator was then rotated at any desired speed, and any slight motion of the electrometer needle allowed to subside. The shutter was then opened (so that  $\alpha$  rays could enter the box) and the rate of deflection of the electrometer noted, one observer keeping the speed of the commutator constant while the other took the electrometer readings. A curve showing the variation of the current reaching the electrometer with the rate of rotation of the commutator was thus obtained; the shutter always being closed while the speed of the commutator was being changed from one value to another. Whenever it was necessary to "earth" the quadrants the commutator was stopped and the above procedure repeated. When the whole curve had been obtained the test for leak was repeated, and if any was found the curve was rejected.

*Alterations in the Apparatus and Method.*

(1) *Variation of the Form of the Flash of Ionisation.*—In some of the earlier readings the flash of  $\alpha$  rays entered the box through two narrow slits instead of through the single slit S and the aluminium covered mica window  $m$  shown in fig. 2. The upper slit was in the plane of the upper surface of the plate B (instead of the window  $m$ ), and the other one was about 5 mm. lower down and slightly to one side so that the beam of  $\alpha$  rays entered the box obliquely. The purpose of the obliquity was to avoid any effect on the measured mobility of the slight distortion of the field, produced by the upper slit. This arrangement was found to be unsatisfactory owing to the gradual diffusion through the top slit of some of the ions produced by the flash between the two slits. It was shown that this effect while it made no difference to the position of the maximum of the "peaks" obtained, prevented the curves falling properly to the axis on the low frequency side, as might be expected. (The effect would, of course, be inappreciable were it not that the currents reaching the electrometer, even at the maximum of the peak, are extremely small.) The arrangement shown

in fig. 2 and described above was therefore substituted; the results obtained with this earlier form of the apparatus are, however, of some interest since the form of the flash of ionisation in the two cases will obviously be very different. The fact that the values for the mobility are the same confirms the view that no very serious error has been introduced into the mathematical treatment given above by the assumption that  $q_x$  is a constant during the flash.

(2) *Introduction of a Gauze.*—Owing to the inductive action of the alternating field on the electrometer the average potential of both pairs of quadrants is considerably different from that of earth; consequently a very slight defect in the insulation may produce a motion of the electrometer needle comparable with that due to the current which is being measured.

This has been eliminated by previous investigators with the alternating field by introducing a gauze below the electrode and maintaining a constant field between the two. The gauze takes the inductive action, but ions of the appropriate sign pass on to the electrometer. In certain cases this method was also adopted in the present work.

A sheet of perforated zinc, with holes of diameter  $\frac{1}{16}$  in., was used, about 1 cm. below the electrode A. It was then possible to dispense with the condenser C and to keep the second pair of quadrants permanently connected to earth. The introduction of the gauze also had the advantage that it prevented ions of the opposite sign to those dealt with from reaching A at any frequency. The distorting action of the gauze on the field was minimised by making all three fields (the two phases of the alternating field and the steady field from the gauze to A) almost exactly equal. It was felt, however, that the absolute values obtained for the mobility would be more accurate when no gauze was used (since there could then be no distorting action of this kind). The values given later (in Table I) were all obtained with no gauze. The gauze may, however, be very conveniently introduced when it is desired to compare mobilities (since any distorting action will be constant if the fields are kept the same), and examples of its use are given in Part II of this paper.

#### *Corrections.*

(a) *Distortion of the Field by the Ions.*—A correction for the effect of "space charge" is usually necessary in measuring mobility. To determine the extent of the correction in this case, the density of ionisation between the plates was varied by varying the width of the slit through which the  $\alpha$ -rays entered. The position of the "peak" was found for each width of slit, the humidity being kept constant, and the limiting position for zero width was found by extra-

potation. By taking a large number of curves it was found that the correction (under the conditions of the curves from which Table I was obtained) amounted to nearly 1 per cent.; it could not be determined with accuracy, being of the same order as the experimental error.

(b) *Distortion of the Field by the Walls.*—To determine the correction to be applied for this the distance between the plates was varied, and the limiting value obtained for the mobility when the plates approached each other was taken as the true value. The correction (under the conditions of Table I) was found to amount to about 5 per cent.

(c) *Corrections for Temperature and Pressure.*—The values obtained were reduced to 15° C. and 760 mm. on the assumption that the mobility varies directly as the absolute temperature and inversely as the pressure. The temperature was read from a thermometer, the bulb of which projected into the mobility box, and the pressure from a barometer in the laboratory.

#### Experimental Results.

In all cases it was found that the negative ions gave only one peak in the range of mobilities investigated (*i.e.*, from about 0.4 to 4.0 cm. per second per volt per centimetre). Fig. 3 shows typical examples of the curves obtained

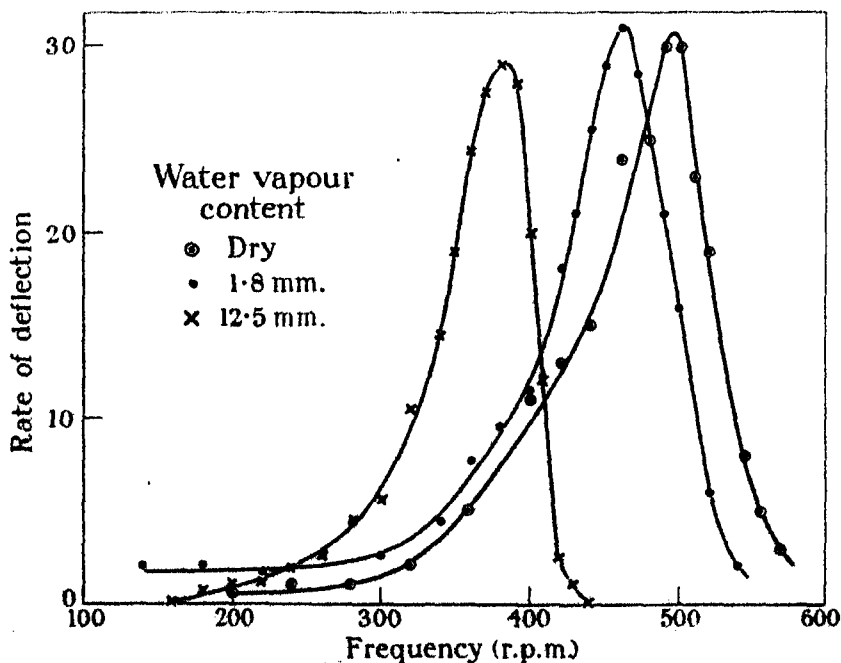


FIG. 3.

at three different humidities. The general form of the curves was not influenced by the introduction of a gauze, except for the fact that when there was no gauze present the curves fell below the axis at the extreme ends, owing to the arrival at the electrometer of positive ions. The curves in fig. 3 were taken with the gauze present; these are shown for convenience in comparing the results for negative ions with those for positive ions under exactly similar conditions; the corresponding curves for positive ions are given in Part II, and the reasons why a gauze was necessary when working with positive ions are also given there.

The peak was found to move gradually towards the current axis as the humidity was increased, showing a gradual fall in mobility. A number of values obtained at different humidities are given in Table I, which refers to determinations made under the following conditions:—Distance between plates, 7.90 cm.; advancing voltage, 657; retreating voltage, 495;  $\alpha$ , 0.345. The values given in the last column are calculated from the mean frequencies after making small corrections for the atmospheric pressure and temperature and for changes in the advancing voltage.

Table I.

Pressure of H <sub>2</sub> O. (mm.)	Peak Frequencies.	Mean.	K (corrected).
0.01	446, 434, 441, 432	438	2.15
0.05	436, 431, 434, 436	434	2.15
0.15	430, 432, 433, 432	433	2.10
0.20	427, 430, 432, 426	428	2.07
0.60	434, 433, 436, 430	433	2.09
2.4	400, 407, 403, 407	404	1.98
4.8	387, 382, 383, 386	384	1.87
6.4	392, 383, 388, 390	388	1.90
8.5	358, 356, 352, 358	356	1.76
9.5	366, 367, 362, 368	366	1.82
12.0	359, 355, 355, 348	354	1.73
14.8	347, 343, 345, 345	345	1.68
16.5	335, 330, 333, 325	331	1.60

It will be seen that when the curves obtained at a given humidity were repeated a number of times the extreme difference between determinations of the position of the peak was always less than  $3\frac{1}{2}$  per cent.

Fig. 4 shows the variation of mobility with amount of water vapour present, the values being taken from Table I.

The conditions of the experiment were altered several times (chiefly in attempts to increase the "resolving power" of the apparatus; though actually no curves very much sharper than those given in fig. 3 were obtained). The

strength of field used varied from about 50 volts/cm. to about 200 volts/cm., and the age of the ions (when they struck the top plate) from about 0.1 second to about 0.02 second.

No change of mobility greater than the experimental error was observed either with age or with strength of field.

*Discussion and Conclusions.*

Upon the numerous experimental results on mobility which have accumulated during the past 25 years, theoretical speculation has been rife despite the fact that a number of the observations are mutually inconsistent. A study of the literature indeed leaves one with an impression of some chaos in our information on the subject.

The writers, therefore, feel that it is premature to attempt any theoretical

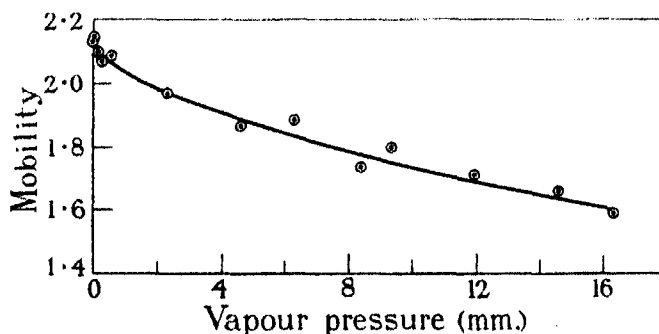


FIG. 4.

explanation of their results until a careful redetermination of other properties of ions in gases has been made. Certain conclusions, however, may be drawn from the results they have obtained.

It will be seen from Table I that in the driest air available the value of mobility obtained was 2.15 in agreement with the more recent values of Loeb, and higher than those obtained by the early investigators. With the addition of water vapour the curve of mobility with vapour pressure falls rapidly at first, and then more slowly reaching a value 1.60 in saturated air, not far from Zeleny's value 1.51.

It has usually been stated that the mobility of negative ions in air is lowered by water vapour, but that the positive ions are little affected; and on the cluster theory of ionic structure it seemed likely that this might ultimately be correlated with the fact that, on the expansion of wet air, the negative ion



acts as a nucleus for condensation at a lower degree of supersaturation than the positive ion. The writers extended their mobility measurements to saturated air to see whether there was any marked drop in the mobility vapour pressure curve in this region which might be taken as evidence of an incipient condensation becoming marked at this stage. No evidence of any drop was obtained. The information recorded in Part II of this paper shows that water vapour is also not without its effect on positive ions of short age, and it is clear that a fuller determination of its comparative effect on the two signs of ion is necessary before any theory is propounded. A further stumbling block is the absence of any definite information on the value of the dielectric constant of water vapour at room temperature as this enters into several mobility formulæ. Until that is known, the possibility that the effect of water vapour on mobility may be mainly due to its effect on the dielectric constant of the medium cannot be entirely excluded.

With reference to the numerical values of mobility, one important conclusion can be reached. In the ordinary alternating field method, if the negative ions are electrons in their early life and change to full ions later, they alter the shapes of the current voltage curve. This raises some doubt whether a mobility calculated from such a curve really gives the true value for a fully-formed ion. The writers' method avoids this possible source of error, because in it every negative ion which has not renounced its electronic state before reaching the bottom plate will be caught by it at frequencies anywhere near the peak frequency, and will therefore not contribute to the current received by the electrometer or affect the position of the peak frequency. This, indeed, is an important advantage that the method possesses, and the value of mobility obtained by it is the true mobility of normal fully formed gas ions. It is not the mean mobility of a group of gas ions mixed with a small percentage of electrons for a portion or the whole of their path. Similarly, the effect of water vapour is a true effect on the ion itself, and not due to a change in any percentage of electrons which, but for the action of the bottom plate, might have been present in the current stream. At the same time the possibility that a given ion in crossing the mobility box passes through numerous changes in molecular aggregation, and that its measured mobility is the statistical average of its mobilities in these successive states, is not excluded. On this point the method gives, of course, no information.

Again, an inspection of the current frequency curves shows that the value of mobility obtained is not the mean value for a number of stable groups differing considerably in mobility. The smoothness of the curve and the

height of the peak and its width, show that at any rate the great majority of the ions are of one single mobility. The presence of any other groups in appreciable quantity between the mobilities 0.4 and 4.0 would be shown by subsidiary peaks. At the same time it must be said that the resolving power of the apparatus is hardly sufficient in general to detect a group contributing less than, say, 5 per cent. of the total ions present. In the neighbourhood of the peak the resolving power is probably still less.

With respect to the effect of field on the velocity of an ion the method is not suitable for investigation except over a limited range. It was found, however, that the velocity of these fully-formed negative ions was proportional to the field in all the measurements made at fields from 50 volts/cm. to 200 volts/cm. This is in agreement with the results of Loeb\* and of Kia Lok Yen† over a far wider range.

For a complete study of mobility at atmospheric pressure the apparatus in its present form has one unfortunate limitation. The necessity of having a very thin window of appreciable area to admit the  $\alpha$ -rays from the revolving polonium prevents the use of a hermetically sealed vessel, from which the last traces of water vapour can be removed. It has not therefore been possible to test the view of Townsend and his collaborators that the "normal" negative ion only occurs when water vapour or other impurities are present, or that of Nolan that it is an *aggregate* of water molecules which decreases in size and increases in mobility as the last traces of vapour are removed.

Some experiments on another form of peak method are now in progress in this laboratory with which the writers are hopeful of success in this region.

#### *Summary.*

An improved absolute method of measuring the mobility of ions in air at atmospheric pressure is described and applied to negative ions.

The method depends upon the production of ions by a series of flashes of  $\alpha$ -rays and their subjection to an alternating field of a special kind. The conditions are so arranged that when the current arriving at an electrometer is plotted with frequency of the alternating field a curve with a sharp peak is obtained, the position of which gives an accurate measurement of the mobility. The method gives the mobility of fully formed negative ions, since the results are not influenced by ions which preserve their electronic state after birth for any appreciable portion of their path in the field.

\* Loeb, 'Proc. Nat. Acad. of Sci.,' vol. 2, p. 345 (1916).

† Kia Lok Yen, 'Proc. Nat. Acad. of Sci.,' vol. 4, p. 91 (1918).

The effect of water vapour on the mobility of negative ions has been studied over a wide range of humidity. In reasonably though not exceedingly dry air the value obtained is 2.15 cm./sec./volt/cm. in fields from 50 to 200 volts/cm. This is higher than that of early investigators, but is in agreement with Loeb's more recent value. With the addition of water vapour the mobility falls rapidly at first and then more slowly to the value 1.60 in saturated air.

The absence of subsidiary peaks in the curve shows that at any rate the great majority of the ions are of one kind. No other groups were detectable with the resolving power and range of frequency available.

The authors are indebted to the University of Bristol Colston Research Society for a grant in aid of the work.

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*The Mobility of Ions in Air. Part II.—Positive Ions  
of Short Age.*

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(Communicated by Prof. A. P. Chattock, F.R.S.—Received November 12, 1925.)

Until recently far more attention has been given to the problem of the mobility of the negative ion than to that of the positive since the phenomena relating to the latter appeared to be simpler and already well defined. The position has, however, been modified by the interesting discovery by Erikson\* of the existence of two types of positive ions in a given gas, namely initial ions of short age and final ions of lower mobility formed by their later transformation. Evidence of the existence of these two types has also been obtained since by Wahlin.†

The method adopted by Erikson involved the use of a blast of gas of high velocity, of the order of 2000 cm. per sec., in order to obtain the shortage necessary. He found that the initial positive ions had a mobility which could not be distinguished from that of negatives, and that in the case of air this held whether he used air saturated with water vapour or air previously dried by passage over calcium chloride.

\* Erikson, 'Phys. Rev.', vol. 20, p. 116 (1922), and vol. 24, p. 502 (1924).

† Wahlin, 'Phys. Rev.', vol. 20, p. 267 (1922).

Since (as has been shown in Part I), the mobility of negative ions in air gradually falls as water vapour is added, Erikson's results implies that the mobility of initial positive ions is affected by water vapour in exactly the same way as negatives, whereas before this differentiation into initial and final ions had been made it was customary to state that the positive ion in air at atmospheric pressure is little affected by water vapour. But the writers feel some doubt as to the efficiency of the method of drying the large volume of air necessary for a blast of this magnitude. For this reason, and because of the general importance of the result, it was decided to apply to the problem the method of measuring mobility given in Part I.

By varying the applied fields and the distance between the plates the interval of time between the production of the ions and their arrival at A, and hence their age, may be varied within certain limits. Owing to the high alternating fields necessary for short ages, and the consequently large induction effect, the form of the apparatus in which the electrode A (fig. 1, Part I) is protected by a gauze was used in all the experiments.

This method of varying the age is unfortunately not very satisfactory, because transformation of initial ions into final ions is going on continuously while the measurement is in progress. As a method of separating the two types of positive ion it is, therefore, not so good as Erikson's method, in which the ions are aged first and then cross the measuring vessel in negligible time. But the present method is without some of the disadvantages of any gas flow method, particularly in that it permits of a simple humidity control.

By using a high field and a short distance it was hoped to obtain an age so short that the transformation *en route* into final ions is too small to influence the position of the peak due to initial ions. If this can be done an accurate determination of the mobility of *initial* positive ions is then possible.

Several ages were selected and measurements were made in air of different humidities. The results for two of these are given below.

In the first of these the age of the ions when they reached the gauze was about 0.015 to 0.02 sec. obtained by an advancing field of about 200 volts/cm., and a distance of 5.0 cm. between the plate B and the gauze. The results are shown in fig. 1 for three humidities, these being chosen so as to afford comparison with the corresponding results for negative ions given in Part I.

For convenience the position of the corresponding negative peaks is indicated by arrows in the graph. For air containing 12.5 mm. water vapour, it will be seen that the positive and negative curves are practically of the same shape (see fig. 2, Part I) and with their peaks within experimental error at the same

position. Under these conditions it may therefore be definitely stated that the mobility of initial positive ions and negative ions are the same, and at this age very few final ions have appeared.

At the small humidities the results shown in the graph are different. The positive and negative peaks are not in the same position while the positive maximum is broader than the negative, particularly in air dried to the maximum extent that the apparatus permitted. This is what one would expect if a transformation of initial ions into final ions is taking place more or less con-

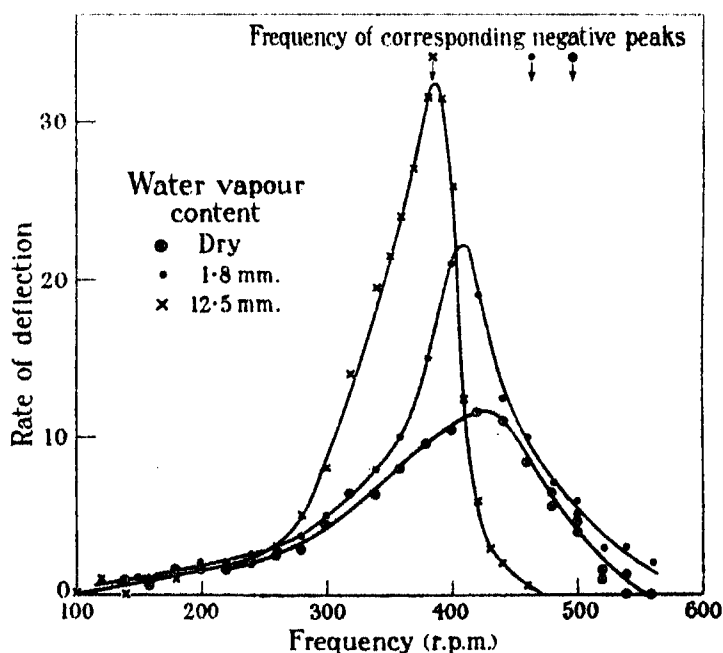


FIG. 1.

tinuously *en route*. The maximum would no longer occur at the frequency which gives the initial ion, but at a lower frequency depending upon the average rate at which transformation is proceeding. The increase in the width of the peak and in the displacement of its maximum as the air is dried brings out an important point, namely, that the rate of transformation of initial ions into final ions is much more rapid in dry air than in wet air.

The fact that the positive curve is so much lower than the corresponding negative curve in dry air affords further evidence of this. The age is such that in wet air few of the positive ions have time to transform, and the positive and negative peaks are almost identical. But if in dry air an appreciable number of

the positive ions are transforming while they cross the box it is easily seen that this will result in a difference in height of the two peaks. Consider ions which at the peak frequency are in their initial state for most of their journey towards B, and in their final state in the subsequent journey towards A. Had they remained as initial ions instead of transforming they would have just missed B and just reached A. As it is, even if they miss B they will fail to reach A because of their reduced mobility. Also, at any lower frequencies they will strike B and be lost. In this way those ions transforming at about this age do not reach the electrometer at all, so that the positive peak is lower than the corresponding negative peak.

In order to obtain the true mobility of initial ions in dry air, the experiments were repeated with the shortest age which it seemed possible to obtain with the present form of apparatus, namely, about 0.007 sec. on reaching the gauze. This was obtained by using a very short insulated sector on the commutator about  $\frac{1}{2}$  inch long, and decreasing the distance between the bottom plate and the gauze to about 3.0 cm.

A typical curve for dry air under these conditions is shown in fig. 2

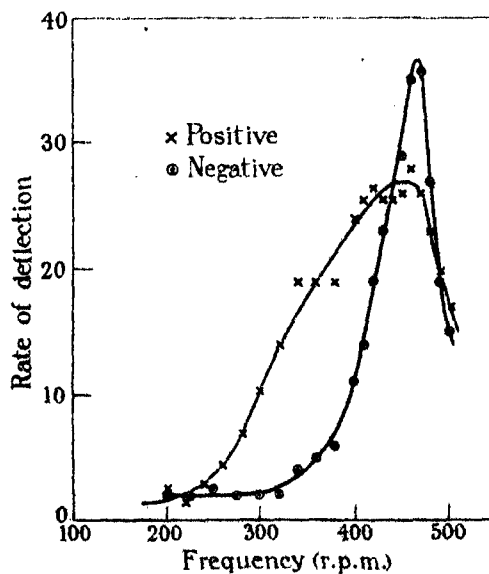


FIG. 2.

(crosses), the corresponding negative curve being shown with circles. As might be expected with the very short insulated sector used, marked fluctuations in readings occur; that these are spurious was shown by the fact that they did

not repeat in other determinations. But in the positive curve the sharp drop on the right of the maximum was found in every case, and this strongly suggests the presence of a large number of initial ions of mobility given by the junction of the tangents to the curve on each side of the maximum. The value of mobility obtained in this way is practically the same as that of negative ions.

A comparison of the left-hand sides of the positive and negative curves shows that even at this short age some transformation of positive ions has taken place and that its amount is probably comparable with that occurring in wet air at four times the age.

Further evidence in favour of the view that the transformation is quicker in dry air was obtained by a slight modification of the method described in Part I, which really amounts to a conversion of the method into one of the Langevin type. The wheel W (fig. 2, Part I) was lowered so that the  $\alpha$ -rays only penetrated a few millimetres above the window, and the wheel was turned with respect to the commutator so that the flash of ionisation occurred during the beginning of the advancing phase of the field. It will at once be seen that below a certain frequency all the ions produced during a flash will cross to the electrode A (or to the gauze) during the advancing phase of the field. While the number of flashes per second varies directly as the frequency, the duration of each flash (and, therefore, the number of ions produced) varies inversely as the frequency. The current-frequency curve is therefore a horizontal straight line at low frequencies. Above a certain frequency no ions cross. The curves will therefore be in the form of "steps" instead of "peaks."

Some curves so obtained are shown in fig. 3. Curves A and B give the results for positive and negative ions respectively in dry air, and curves C and D corresponding results in wet air of humidity 10.5 mm. The distance between the gauze and the bottom plate was 5.0 cm., and the advancing voltage was about 900 volts, so that the age of the ions when they reached the gauze was of the order of 0.012 sec. As will be seen, the steps obtained are not very sharply defined, owing chiefly to the thickness of the layer of ions produced and to the finite duration of the flash, but their general form is what is to be expected from the previous results. For instance, in the wet air the curves C and D practically coincide, that is to say, the positive ions are practically all initial ions of the same mobility as the negatives. But in dry air curve A shows, at any rate, a large number of positive ions of mobility lower than that of the negatives of curve B.

Since the top of the step is not sharp, an accurate value of the ratio of the negative to the positive mobility cannot be obtained from the ratio of the

frequencies in each case. But a rough value can be deduced from A and B by drawing tangents to the curve on each side of the top of the step and noting where they meet. The ratio obtained in this way from the corresponding frequencies is about 1.5, which, if we take the negative mobility as 2.1, gives 1.4 for the mobility of the positive. This is in agreement with the known value for final positive ions, and supports the conclusion from the peak method that in dry air at an age of about 0.015 sec. a large amount of transformation has already taken place.

The conclusion therefore reached is that while this work agrees with that of Erikson in giving the same mobility to negative ions and initial positive

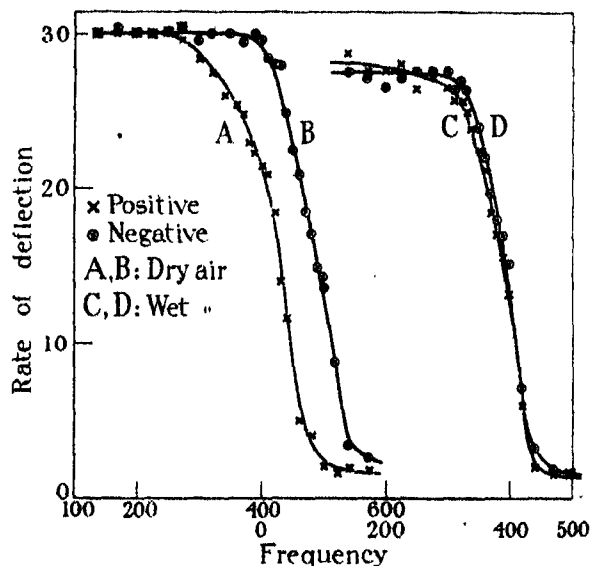


FIG. 3.

ions whether the air is dry or wet, it shows, what Erikson does not appear to have found, that the rate of transformation of the latter into final ions is dependent on the amount of water vapour present. Water vapour affects the mobility of initial positives in the same way as the negatives, and the positive ions so affected do not transform so rapidly into final ions as they do when the water vapour content is reduced. It may be suggested that in Erikson's blast the air was too imperfectly dried to show up the difference in the rate of transformation.

The writers have no definite theoretical explanation of this effect to offer. Erikson considers that the initial positive ion is a single molecule and the



final ion a double molecule, but Hassé\* advances theoretical objections to his argument. Moreover, it does not seem easy to reconcile it with the humidity results. The possibility that the initial ion is doubly charged and the final ion singly charged can also hardly be entertained. Quite apart from the fact that Millikan, Gottschalk and Kelly, by the oil drop method, found no evidence of the production of doubly-charged ions by  $\alpha$  rays at the moment of expulsion, it would be a strange coincidence if a doubly-charged positive ion had the same mobility as a singly-charged negative ion. There are other possible explanations, but until the reason for the lowering of mobility of either ion by water vapour is more clearly understood any speculation would appear to be premature. Observations in excessively dry air would be particularly useful in this connection as the rate of transformation under these conditions might be so great as to be virtually instantaneous. What is clearly needed is a full investigation over a wide range of age and of humidity, including that of extreme dryness. The writers fear, however, that their existing apparatus cannot be usefully employed any further in this direction.

*Summary.*

The method of the previous paper is applied to the measurement of the mobility of positive ions of short age.

Definite evidence was found of the existence of two types of positive ions, an initial ion and a final ion. The initial positive ion has a mobility which is indistinguishable from that of a negative ion, and which is affected by water vapour in the same way. These results are in agreement with the work of Erikson by another method. The authors find, however, that the presence of water vapour has a retarding influence upon the rate of transformation into final ions. Thus, in ordinary dry air a considerable amount of transformation is noticeable within 0.007 sec. of birth; but in wet air the ions are still nearly all in their initial state at double this age.

These conclusions were confirmed by a modification of the apparatus which converted the method into one of the Langevin type.

Theoretical discussion is postponed until more experimental data are available.

The authors are indebted to the Colston Research Society of the University of Bristol for a grant in aid of the work.

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\* Hassé, 'Phil. Mag.', Jan., 1926.

*A Band Spectrum of Tin Monochloride Exhibiting Isotope Effects.*

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Artillery College, Woolwich.

(Communicated by Prof. H. C. Plummer, F.R.S.—Received November 12, 1925.)

[PLATE 2.]

1. *Introductory.*

The present paper is an extension of the work on the band spectra of chlorides of elements of Groups III and IV already published,\* and deals with a hitherto unrecorded band spectrum developed by the uncondensed discharge through the vapour of tin tetrachloride. In the cases of  $\text{CCl}_4$ ,  $\text{SiCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{BCl}_3$  and  $\text{AlCl}_3$  the uncondensed discharge through the vapour of the chloride alone develops bands which may be ascribed to a chloride of the element, while the addition of oxygen to the vapour results in the suppression of these chloride bands and the development of an oxide spectrum. As results from the present investigation, the addition of oxygen to the  $\text{SnCl}_4$  vapour does not appear to quench the new chloride band spectrum and produce the oxide spectrum recorded by other observers; the analogy between the case of  $\text{SnCl}_4$  and those of the other chlorides mentioned, thus appears at present to be incomplete. The new investigation has, however, led to other very interesting results; for it has been possible to arrange a large majority of the heads of the new tin chloride bands into two systems, to assign vibrational quantum numbers to the bands in each system, to attribute the two systems definitely to tin monochloride,  $\text{SnCl}$ , and to recognise the chlorine isotope effect, and to a less marked extent, the tin isotope effect, which is, of course, more complicated.

Earlier observations of bands associated with tin compounds have been limited to a single band spectrum, namely, that developed under suitable conditions when tin or one of its compounds is introduced into a flame. Investigations up to the year 1912 are summarised by Kayser,† who records grating measurements by Eder and Valenta and Von der Seipen. The bands of this spectrum degrade towards the red, and extend from  $\lambda$  4766 to  $\lambda$  3000.

\* W. Jevons, 'Roy. Soc. Proc.,' A, vol. 106, p. 174 (1924).

† 'Handbuch der Spectroscopie,' vol. 6, p. 522 (1912).

Several opinions have from time to time been held as to the origin of this spectrum. Following Mitscherlich, who first discovered it, Eder and Valenta,\* who observed it under many different conditions, attributed it to an oxide of tin. On the other hand, it was ascribed by Hartley to tin itself, and by Hagenbach and Konen† to the metal or a chloride. One result of the present work is to demonstrate that this spectrum is certainly not due to tin chloride for which a new spectrum has been obtained.

## 2. *Experimental Method and General Results.*

As in the former investigation an uncondensed discharge was passed through the vapour of the chloride, in this case  $\text{SnCl}_4$ , a continuous flow of which was maintained through the discharge tube for the duration of the exposure. Its spectrum was first photographed in two low dispersion spectrographs of quartz and glass respectively, namely, Hilger's E.6, and a constant deviation instrument by the same maker. It was found to contain in addition to the Sn and Cl lines (Plate 2, strip 1), an apparently continuous spectrum in the visible region from about  $\lambda$  4900 to about  $\lambda$  3950, and a band spectrum in the near ultra-violet from about  $\lambda$  3910 to about  $\lambda$  2830. In this region the dispersion of the quartz instrument is very small indeed, being only 23 A.U./mm. near  $\lambda$  2850; and while the main features of the regularity of the distribution of the heads became apparent from the measurements of several small quartz spectrograms, higher dispersion plates were clearly necessary in order to obtain more accurate data. The first order of the concave grating spectrograph previously described‡ was therefore employed; the bands were strongly recorded on a fast plate§ in a 12-hours' exposure (Plate 2, strips 2, 3, 4), the slit-width being slightly greater than would ordinarily be used with brighter

\* J. M. Eder and E. Valenta, 'Atlas Typischer Spektren' (Wien, 1911), p. 17 and the following reproductions:—Bunsen flame with  $\text{SnCl}_4$ , Plate II (10); oxy-coal gas blow-pipe flame with  $\text{SnS}_2$ , Plates V (5), VII (5), and VIII (11); Sn arc, Plates XIX (4) and XXXI (5).

† A. Hagenbach and H. Konen, 'Atlas of Emission Spectra,' English edition by A. S. King (London, 1905), p. 25 and the following reproductions:—No. 98 (flame with tin chloride, showing oxide bands); Nos. 257 and 258 (uncondensed discharge through  $\text{SnCl}_4$  vapour, showing neither the oxide bands nor the chloride bands described in this paper).

‡ W. Jevons, *loc. cit.*, p. 175.

§ Ilford "Monarch" plates were used. In previous work with this spectrograph many disappointments had been caused by the fracture of plates during long exposures, owing to the considerable curvature (radius of curvature of grating 7 feet 9 inches, and of plate, therefore, 3 feet 10½ inches). Messrs. Ilford now supply glass which is considerably thinner and more flexible than the best hitherto available. The risk of fracture of the 10 × 2 inches plates they now furnish for use with this spectrograph is very small indeed.

sources. The disadvantages of the large grain of the faster plate and of the wider slit were easily outweighed by the advantage of the larger dispersion (7.4 A.U./mm.); many more heads were detected and more consistent values of their wave-lengths were obtained than with the small quartz instrument. Even the grating failed, however, to show the line structure of any band. As many heads as possible were measured against iron arc wave-lengths. Not all the bands present, however, were measurable in this way, for a considerable number, though clearly distinguishable midway between the two juxtaposed iron spectra, were not developed at all in either of the overlaps. Further measures of all the heads were, therefore, made with reference to the Sn lines present in the same region, the Sn wave-lengths employed being those given by Arnolds.\* It was found, however, that almost every arc line of Sn was much too heavily exposed to permit of accurate micrometer settings, but that the two first ghosts of the line were sufficiently narrow and of suitable intensity for measurement; the mean of the micrometer readings on these two ghosts was, therefore, used instead of the less consistent reading on the heavy line itself. In each case it was previously ascertained by measurement against the iron lines that the means of the positions of the two ghosts approximated very closely to Arnold's Sn wave-length. The actual error was always negligible compared with the errors inherent in settings on the unresolved band-heads.

Three grating plates were obtained. The second positive nitrogen bands were present in all, but with widely different intensities. On one they were very strong, owing to the fact that one of the tubes used during the exposure developed a leak while unattended. On another they were comparatively feeble, while their intensities on the third were intermediate between the first two. This proved to be fortunate, in so far as the variation of the nitrogen bands independently of the tin chloride bands often facilitated the work of distinguishing between doubtful chloride bands and nitrogen band-structure. Again, electrodes of different metals were employed in obtaining these plates, so that any bands due to a product of the action of the liberated chlorine on the electrodes could be detected; several feeble bands in one plate (Al electrodes) were, in fact, eliminated after comparison with the other two (Pt and Fe electrodes). The final data were obtained from several measurements of these three grating plates, after preliminary measurements of three plates from the small quartz instrument.

It was recognized at once that the new bands fall into two distinct sets

\* R. Arnolds, 'Zeit. f. Wiss. Phot.,' vol. 13, p. 313 (1914).

differing sharply from one another, as is apparent from Plate 2, strip 1. In the less refrangible set comparatively few bands have been observed; these degrade towards the red and extend from  $\lambda$  3486 to  $\lambda$  3910, *i.e.*, almost to the violet limit of the continuous spectrum which invariably accompanies the new bands. The more refrangible set, on the other hand, consists of a large number of single bands regularly distributed over the region  $\lambda$  2830 to  $\lambda$  3405 and degraded towards the further ultra-violet. The paper is mainly concerned with the latter set, but certain data obtained for the less refrangible set are also recorded.

### 3. *The More Refrangible Bands; Classification into Systems $\alpha$ and $\beta$ .*

The more refrangible bands (region  $\lambda$  3405– $\lambda$  2830) are those to which the chief interest is found to attach. Two of the main features of these bands were apparent from the small dispersion plates alone (Plate 2, strip 1). In the first place, the more prominent heads occur in two regions separated by a middle region of rather closely-packed bands of relatively low intensities, thus suggesting a possible sub-division of the whole set of bands into two systems which partially overlap in the middle. The other noticeable feature was the frequent recurrence of three approximately constant intervals between the wave-numbers of the heads; namely, one interval of 425, another of about 345, and the third so near to the difference of the other two, *viz.*, 80, as to suggest the possibility of arranging the wave-numbers in a single table consisting of rows and columns of approximately equidistant bands. In such a table the interval 345 would recur between successive wave-numbers in a given row, and the interval 425 between those in a given column. In the Deslandres table for a band system of the usual type an arithmetical progression of first differences occurs between wave-numbers of consecutive heads in a row, or in a column, or in a diagonal; in the table suggested each of these progressions would be replaced by a series of intervals which are apparently constant.

The following three results are obtained by setting out, in the manner described, the data (Table I) finally obtained from the grating plates: (i) It is impossible to include all the observed heads in *one* such table, but, with a few exceptions, they may be disposed in *two* similar tables, one (Table II $\alpha$ ) comprising the less refrangible bands of the set, and the other (Table II $\beta$ ) the more refrangible, with a small overlap in the middle region of low intensities. Any attempt, by extrapolation, to unite the two tables involves, not only an unduly large number of gaps corresponding to unobserved bands, but also the use of wave-number intervals differing from those already mentioned by amounts

far in excess of the errors of observation. (ii) Each table embraces one of the two regions of high intensities to which attention was first drawn; the distribution of intensities is, in fact, remarkably similar in the two tables. (iii) There is a significant general tendency, shown in both tables, for the first differences to decrease from left to right in a row, and from top to bottom in a column; though the data are not sufficiently accurate for importance to be attached to the magnitude of individual second differences.

Allowing, then, for the observational errors inherent in all measurements of the heads of unresolved bands, which are increased in the present case, as will be shown later (Section 6), by the multiplicity of tin isotopes, it appears that the more refrangible set of bands consists mainly of two partially overlapping systems,  $\alpha$  and  $\beta$ , of the Deslandres type, closely resembling one another in intensity distributions, in the magnitude of the first differences, and in having second differences so small that their constancy has not been established. Only a few comparatively weak bands remain outside these two systems; these form the subject of a later section of the paper (Section 6).

The two systems are each of the simple type which the quantum theory of band spectra associates with a molecule which is diatomic. Since the conditions of its production indicate that the spectrum is due to a chloride of tin, it would appear that the molecule responsible for both systems must be tin monochloride,  $\text{SnCl}$ , a molecule which is, of course, not known in chemistry and is, no doubt, unstable.

#### *4. Assignment of Vibrational Quantum Numbers to Band-heads of Systems $\alpha$ and $\beta$ .*

It is convenient at this stage to quote\* very briefly a few points of the quantum theory of band spectra which find application in the present analysis.

The total energy of a molecule is regarded arbitrarily as the sum of three parts; the electronic energy,  $E^e$ , the energy of nuclear vibration,  $E^v$ , and the energy of molecular rotation,  $E^m$ ; that is

$$E = E^e + E^v + E^m, \quad (1)$$

\* Using the notation given by R. S. Mulliken, to whose recent series of papers on "The Isotope Effect in Band Spectra" frequent reference will be made. In order to avoid repetition, use will be made throughout of Mulliken's own numbers for these papers in the 'Physical Review' (1925):—I, vol. 25, p. 119 (Theory); II, vol. 25, p. 259 (BO); III, vol. 26, p. 1 (CaI); IV, vol. 26, p. 319 (SiN).



+ 2	0 2 1 3 2 4 3 5	71.5	5	30558 30641.1 30721 30809	- 1.5 - 1.3 + 5.9	(iii)	36.4 28.7 21.0	4 2 0?	32924 33008 [33178.7]	- 0.6 - 1.3 - 2.0	66 71
+ 1	0 1 1 2 2 3 3 4 4 5	34.4 26.0 09.7 01.5	7 2 2 1	30809 30889 [31068.8] 31147 31226	- 1.0 - 0.6 - 0.6 0.0	(iv)	04.5 2997.1 90.0 82.3 75.3	6 2 0?? 2 0	33274 33356 33435 33521 33600	- 1.6 + 1.3 - 2.0 + 1.7 - 1.6	65 67 74 74
0	0 0 1 1 2 2 3 3 4 4 5 5	3197.8 90.0 82.2 81.9 66.7	7 2 0? 3 1	31262 31339 31476 31419 [31494.1] 31569	- 0.5 - 1.1 + 1.9 + 1.7 - 1.5	(v) (vi)	73.4 66.3 59.6 59.3 52.5 45.3 38.8	8 3 2 5 3 0? 00?	33622 33702 33779 33782 33860 33942 34019	- 0.6 - 0.5 + 0.1 - 0.4 - 2.3 - 0.2 - 3.1	60 63 63 63 73
- 1	1 0 2 1 3 2 4 3	55.2 54.5 47.1 32.4	2 7 2 0??	31684 31692 31766 [31842.6] 31915	+ 0.4 - 0.6 - 1.8 - 2.0	(vii)	36.7 35.8 29.1 15.9	3 10 3 0	34042 34052 34130 [34207.7] 34285	- 1.6 - 0.7 - 0.2 - 0.2	58 60 64 70
- 2	2 0 3 1 4 2	14.0 12.4 07.5 05.2 3098.2	0? 5 0? 4 0?	32163 32190 32171 32195 32267	+ 0.5 - 0.3 - 2.9 + 1.9 + 1.5	(viii)	00.7 2899.4 95.0 93.0 87.0	2 7 2? 5 2?	34464 34480 34532 34566 34628	+ 1.5 - 0.4 - 4.1 + 0.5 - 2.6	61 60 67 61 61
- 3	3 0 4 1	74.1 71.6 65.0	0 1 2?	32520 32547 32617	+ 1.0 + 1.4 + 1.0		65.8 58.4	1? 1	34884 [34905.7] 34974	+ 5.0 - 4.4	64 57
- 4	4 0			[32968.5]		(ix)	29.7	0	35329	+ 0.4	(xii)





System $\beta$ .								
$n'$	0	1	2	3	4	5	6	7 8
0	(8) 33623 348 33274 350 33924 342 33583 347 32235 336 31899 430 428 432 426 426 435 429							
1	(10) 34063 350 33702 346 33356 348 33008 338 32670 342 32328 338 31990 428 428 428 426 427 422 428 424							
2	(7) 34480 350 34130 348 33782 347 33435 343 33092 336 32756 342 32414 334 32080 426 426 425 425 425 429 422 430 422							
3	xl. (5) 34556 418 418 425 425 421 34556 418 418 425 425 421							
4	(0) 35339 355 34974 346 34638 343 34285 343 33942 342 33600 xii. 419							
5	xiii. 34019							

## NOTES (TABLES I AND II).

[ $\nu_{\text{calc.}}$ ] Head not observed. Wave-number from formulae  $10, a$  and  $10, \beta$ . x. A very doubtful head was measured on one plate only at  $\lambda$  2922.5, inserted.

? Doubtful head. ?? Very doubtful.

i. Masked by Nitrogen Second Positive Band  $\lambda$  3371.

ii. Near Sn  $\lambda$  3283.5,  $\nu$  30447. A very doubtful head was measured on one plate at  $\lambda$  3282.4, (01?),  $\nu$  30457.

iii. Near Sn  $\lambda$  3262.338,  $\nu$  30653.5.

iv. Near Sn  $\lambda$  3218.690,  $\nu$  31059.6.

v. Near Sn  $\lambda$  3175.039,  $\nu$  31486.6.

vi. Position occupied by Nitrogen Second Positive Band  $\lambda$  3150.

vii. Near Sn  $\lambda$  3141.823,  $\nu$  31819.5.

viii. The same head has been inserted in two positions:—SnCl $^{37}$   $a$  (3, 1) and SnCl $^{38}$   $\beta$  (3, 8).

ix. Near Sn  $\lambda$  3032.783,  $\nu$  32963.5.

xi. Near Sn  $\lambda$  2863.320,  $\nu$  34914.3.

xii. Measured on Quartz Prism Spectrograph plates only; not detected in Grating plates.

xiii. Four doubtful heads were measured on one Grating plate as follows. They could be included in Table II by extending the range of  $n'$  to 6, but are not considered sufficiently certain to justify this extension:—

$\lambda$ 2879.8	Int.	0 ??	$\nu$ 34714	$n' = 5$	$n'' = 3$
45.0	0 ?	0 ?	35139	6	3
24.3	0 ?	0 ?	35397	5	1
17.0	00 ?	00 ?	35474	6	2

xiv. Position occupied by Sn  $\lambda$  2850.618,  $\nu$  35060.8.

where the affixes  $e$ ,  $n$  and  $m$  represent the quantum numbers pertaining to the respective states.

The wave-number *in vacuo* of any emitted line of a band system is given by

$$\nu = (E' - E'')/hc, \quad (2)$$

where  $E'$  and  $E''$  are the total energies of the molecule before and after a transition from a more excited to a less excited state,  $h$  is Planck's action constant, and  $c$  the velocity of light *in vacuo*. In the most general case the change in  $E$  involves simultaneous changes of  $E^e$ ,  $E^n$  and  $E^m$ , the first of these being, like  $E' - E''$ , positive in the case of emission, and the other two either positive or negative.

Then

$$\begin{aligned} \nu &= (E'^e - E''^e)/hc + (E'^n - E''^n)/hc + (E'^m - E''^m)/hc \\ &= \nu^e + \nu^n + \nu^m, \end{aligned} \quad (3)$$

$\nu^e$ ,  $\nu^n$ , and  $\nu^m$  being regarded as electronic (positive) vibrational (positive or negative) and rotational (positive or negative) parts of  $\nu$  (positive).

The origin of a band is such that  $\nu = \nu^e + \nu^n$ ,  $\nu^m$  being zero; while the origin of a band-system is defined by  $\nu = \nu^e$ , both  $\nu^n$  and  $\nu^m$  being zero, i.e., it is the origin of the particular band given by  $\nu^n = 0$ . Hence  $\nu^n$  is the separation of the origin of any band from the origin of its system ( $\nu^e$ ); while  $\nu^m$  for any line of a band is the separation of that line from the origin ( $\nu^e + \nu^n$ ) of the same band.

Writing for the vibrational energy the approximate expression\*

$$E^n = hc(an - bn^2), \quad (4)$$

we have

$$\begin{aligned} \nu^n &= (E'^n - E''^n)/hc \\ &= (a'n' - b'n'^2) - (a''n'' - b''n''^2), \end{aligned} \quad (5)$$

where  $n'$  and  $n''$  are the vibrational quantum numbers for the initial and final states.

The origins of all the bands in a system are then given by

$$\nu = -\nu^e + (a'n' - b'n'^2) - (a''n'' - b''n''^2) \quad (6)$$

\* Using two terms only of the expansion

$$W_0^n = nh\nu_x(1 - nx \dots)$$

(See A. Kratzer, 'Zeit. f. Phys.,' vol. 3, p. 207 (1920); or A. Sommerfeld, 'Atombau und Spektrallinien,' 4th edition, p. 714), where  $W_0^n$  is, of course, identical with Mulliken's  $E^n$ ;  $\nu_x$  is the frequency of vibration of the nuclei and is equivalent to  $ac$  in equation (4) and  $x$  is a small constant ( $= 0$  if the vibrations are simple harmonic) corresponding to  $bc/\nu_x$  in equation (4).

with appropriate numerical values for  $n'$  and  $n''$  ( $n' = 0$ , and  $n'' = 0$  for the *system origin*); and the *heads* of the bands by

$$v = v^e + v_{\text{head}}^m + (a'n' - b'n'^2) - (a''n'' - b''n''^2) \quad (7)$$

where the rotational part  $v_{\text{head}}^m$  is the separation of the *head* of the band from its *origin*. This separation is not constant throughout the system, but varies from band to band, *i.e.*, it is a function of  $n'$  and  $n''$ . The function involves a comparatively large constant term  $\kappa$ , and other terms in  $n'$ ,  $n'^2$ , ...,  $n''$ ,  $n''^2$ , ..., and  $n'n''$ , ....

In representing the heads of either system of SnCl bands we may neglect the variable part of  $v^m$  and retain only the constant part  $\kappa$ , as the errors so introduced will be within the limits of error of the measurements of the unresolved heads. We shall then have for the heads of the two systems  $\alpha$  and  $\beta$  :—

$$\begin{aligned} v_\alpha &= (v_a^e + \kappa_a) + (a_a'n' - b_a'n'^2) - (a_a''n'' - b_a''n''^2) \\ v_\beta &= (v_\beta^e + \kappa_\beta) + (a_\beta'n' - b_\beta'n'^2) - (a_\beta''n'' - b_\beta''n''^2) \end{aligned} \quad (8)$$

It is first necessary to assign quantum numbers  $n'$ ,  $n''$  to the initial and final states of nuclear vibration concerned in the emission of each band. Certain well-established simple rules enable this assignment to be made, at least provisionally. Taking a column of either system in Table II, it will be observed that in many cases the intensities increase as we go upwards, the band in the top row being the strongest. This band, therefore, is probably associated with the minimum value of one of the quantum numbers,  $n'$ ,  $n''$ ; for following the general run of the intensities, it would be expected that, if there were a smaller value, the band pertaining to it would be fairly strong, and so could not have escaped observation. A similar argument, applied to the intensities in a row passing from right to left leads to the assignment of the minimum value of the other quantum number to the bands in the left-hand column. Thus the top-left-hand member ( $v$  31262 in  $\alpha$  and  $v$  33622 in  $\beta$ ) is associated with the minimum values of both  $n'$  and  $n''$ . It is simplest to assume that each of these is zero, and that the other values are successive integers\* increasing to the right and also increas-

\* Though such numeration applies to most systems dealt with by the theory, it may be that half-integral values of  $n'$  and  $n''$ , starting from  $\frac{1}{2}$  in each case, should be used; there is no way of deciding here with the available data. Very accurate observations of an isotope effect would settle the question, as Mulliken (II, p. 279) has shown in the case of BO—the only case where there is real evidence as yet that half-integral values are probable.

ing downwards. Since an increase in  $\nu$  must accompany an increase of the initial quantum number  $n'$  while  $n''$  remains constant, and also a decrease of  $n''$  while  $n'$  remains constant, it is clearly  $n'$  which increases downwards from row to row, and  $n''$  which increases horizontally from column to column in each of the Tables (II $\alpha$  and  $\beta$ ). Thus in system  $\alpha$   $n'$  and  $n''$  range from 0 to 4 and from 0 to 9 respectively, and in system  $\beta$  they range from 0 to 4 (or, possibly, 5) and from 0 to 8 respectively.

Some support for the above choice of the (0, 0) band in each system is derived from a consideration of the first differences. These decrease with increasing values of  $n'$  and  $n''$ , as they should in general, since the inharmonic nature of the vibrations, which finds its expression in  $n'^2$  and  $n''^2$  terms, normally causes decreases of first differences; no certain case is known where there is an increase. Further support is gained from an examination of any one of the diagonal groups of bands characterised by a constant change of vibrational quantum number, *e.g.*, the group 33274 (0, 1),  $\nu$  33356 (1, 2),  $\nu$  33435 (2, 3),  $\nu$  33521 (3, 4),  $\nu$  33600 (4, 5) in system  $\beta$  having  $n'' - n' = 1$ . Birge\* has pointed out that, as a general rule, the quantum numbers in any such group increase in the direction in which the bands themselves are degraded. The numeration in the present case obviously conforms with this rule, for the values of  $n'$  and  $n''$  in the above group increase with wave-number, and the bands of both systems are degraded towards higher wave-numbers. Still further support is afforded by the Cl isotope effect described in a later section, although it is not accurate enough to decide between integral and half-integral values.

The values of  $n'$ ,  $n''$  and the change  $n'' - n'$  for each band are inserted in Table I, which gives the data for both systems. Several of the gaps in Tables I and II, corresponding to unobserved bands, may be due to the proximity of heavy Sn arc lines or their ghosts, as noted in the tables; generally, it was felt that observations in the space between a heavy line and either of its ghosts were of little worth, and they have accordingly been omitted. A probable explanation of the few remaining gaps is that, in each (diagonal) group of neighbouring bands, the first band is both stronger than, and also degraded towards, the succeeding ones, which are, therefore, either partially or entirely masked by its (unresolved) structure. Thus in the most heavily exposed grating plate, none but the very strong head  $\nu$  34052 (1, 0) was definitely

\* R. T. Birge, 'Phys. Rev.', vol. 25, p. 240 (1925) (Abstract No. 23 of paper before American Phys. Society). See also R. S. Mulliken (III, p. 17). R. Mecke ('Zeit. f. Phys.', vol. 32, p. 823 (1925)) has discussed the matter in detail, and has sought quantitative as well as qualitative relations.

observed in the  $n'' - n' = -1$  group in system  $\beta$ ; (2, 1) being completely masked by (1, 0), and (3, 2) and (4, 3) being very doubtful. In a less dense grating plate, however,  $\nu$  34130 (2, 1) was unmistakable, and  $\nu$  34285 (4, 3) certain enough for inclusion in the tables, leaving only (3, 2) excluded as uncertain.

The estimated intensities of the bands in Systems  $\alpha$  and  $\beta$  are shown in ( ) in Table II. Intensities of like-numbered bands in the two systems are of about the same order,  $\beta$  being perhaps very slightly the stronger system on the whole: the region occupied by the two systems is so restricted that variation of plate sensitivity may probably be ignored. Further, the distributions of intensities are very similar in the two systems. This is expected from the close similarity of the first differences (and, therefore, of the vibrational energy constants, which are discussed in the next section, see equations  $10_1\alpha$  and  $10_1\beta$ ). The distribution in each system is of a fairly normal type, some broad features of which are as follows:—(a) A diagonal group ( $n'' - n'$  constant) begins abruptly with a band (having  $n'$  or  $n'' = 0$ ) of higher intensity than the other bands of the group, which decrease in intensity as  $n'$  and  $n''$  increase. An exception occurs in the group  $n'' - n' = 0$  where the band (2, 2) is decidedly stronger than the band (1, 1). (b) The group  $n'' - n' = 0$  is the most intense of the system, and other groups become less intense as their separations from it increase. The two groups  $\pm 1$  are, however, almost as strong as group 0. (c) In system  $\alpha$  the pair of groups  $\pm 1$  are roughly equal to one another in intensity, as are also the pair  $\pm 2$ . This is, so far, in accordance with Lenz's theoretical prediction\* that groups having equal and opposite values of  $n'' - n'$  should be of approximately the same intensity. It is not, however, borne out by all pairs; e.g., in system  $\beta$  the bands of group  $-2$  are appreciably stronger than those of group  $+2$ . (d) More bands are observed for positive than for negative values of  $n'' - n'$ ; Mulliken (III, p. 22) has explained this general tendency in terms of Lenz's theory. The above features have been noted by Mulliken in BO (II, p. 292), CuI (III, p. 22), SiN (IV, p. 334), and by Birge (*loc. cit.*) in other cases. See also SiO, for which Mecke† has assigned vibrational quantum numbers in place of the writer's empirical numeration.‡

\* W. Lenz, 'Zeit. f. Phys.,' vol. 25, p. 299 (1924).

† R. Mecke, 'Phys. Zeit.,' vol. 26, p. 231 (1925).

‡ W. Jevons, *loc. cit.*, pp. 179 and 180.  $n = 77, 76 \dots 72$  is replaced by  $n' = 0, 1 \dots 5$ ; and  $p = 103, 102 \dots 93$  by  $n'' = 0, 1 \dots 10$ .

5. *The Inter-system Separations and the Electronic States of the SnCl Molecule.*

The last column of Table I contains the wave-number intervals,  $\nu_\beta - \nu_\alpha$ , between similarly numbered heads of the two systems. The small variations among these figures are not entirely accounted for by the observational errors; for a general increase of  $\nu_\beta - \nu_\alpha$  is apparent in every group ( $n'' - n'$  constant) in which the observations are sufficiently complete. A further fact about this systematic variation is brought out by Table III, in which  $\nu_\beta - \nu_\alpha$  is set out against  $n'$  and  $n''$ ; namely, that, apart from accidental variations, there is a definite increase of  $\nu_\beta - \nu_\alpha$  with  $n''$  ( $n'$  constant), but no appreciable change with  $n'$  ( $n''$  constant). The means of the values in each column have, accordingly, been inserted at the foot of the table.

Table III.—Separations of like numbered SnCl<sup>35</sup> heads of Systems  $\alpha$  and  $\beta$ ,  
( $\nu_\beta - \nu_\alpha$ ).

$n'' \backslash n'$	0	1	2	3	4	5	6	7	8
0	2360	2365	2366	2372	2370	2369			
1	2360	2363	2367		2376	2377	2378		
2	2360	2364	2363		2371	2377	2379		
3		2361			2377			2381	2390
4		2357	2361	2370	2373	2374			
Mean	2360	2362	2364	2371	2373	2374	2378.5	2381	2390
( $\nu_\beta - \nu_\alpha$ ) <sub>obs.</sub>									
( $\nu_\beta - \nu_\alpha$ ) <sub>calc.</sub> (Eqn. 11)	2360.1	2362.4	2365.1	2368.2	2371.7	2375.6	2379.9	2384.6	2389.7

If the two systems were parallel, the formulæ (8) representing their heads would differ only in the values of the constant term  $\nu^e + \kappa$  and the observed separation  $\nu_\beta - \nu_\alpha$  would be given by  $(\nu_\beta^e - \nu_\alpha^e) + (\kappa_\beta - \kappa_\alpha)$ , containing no vibrational term. The observed increase of  $\nu_\beta - \nu_\alpha$  with  $n''$ , however, will demand different values of one or both of the coefficients of  $n''$  and  $n''^2$ , while the observed independence of  $\nu_\beta - \nu_\alpha$  and  $n'$  implies identical values of the coefficients of  $n'$  ( $a_\alpha' = a_\beta'$ ) and  $n'^2$  ( $b_\alpha' = b_\beta'$ ). The observed separations of like numbered heads will, then, be represented by

$$\nu_\beta - \nu_\alpha = (\nu_\beta^e - \nu_\alpha^e) + (\kappa_\beta - \kappa_\alpha) - (a_\beta'' - a_\alpha'') n'' + (b_\beta'' - b_\alpha'') n''^2, \quad (9)$$

containing a variable vibrational part dependent only on the final state of the molecule. We may assume that the rotational part,  $\kappa_\beta - \kappa_\alpha$ , of the constant term will be negligibly small, since  $\kappa_\alpha$  and  $\kappa_\beta$ , themselves not large, are presumably nearly equal to one another. The constant in equation (9) is then practically the separation of the two system origins ( $\nu_\beta^e - \nu_\alpha^e$ ).

Approximate formulæ\* for the heads of the two systems are :—

$$\nu_\alpha = 31262.5 + 431.3n' - 1.2n'^2 - 353.5n'' + 1.0n''^2 \quad (10_1 \alpha),$$

$$\nu_\beta = 33622.6 + 431.3n' - 1.2n'^2 - 351.4n'' + 1.2n''^2 \quad (10_1 \beta)$$

the residuals ( $\nu_{\text{obs.}} - \nu_{\text{calc.}}$ ) are shown in Table I and are in most cases probably no larger than the errors of observation. The separations of corresponding heads of the two systems is given by the difference

$$\nu_\beta - \nu_\alpha = 2360.1 + 2.1n'' + 0.2n''^2; \quad (11)$$

the values of which are shown at the foot of Table III for comparison with the means of the observed values of  $\nu_\beta - \nu_\alpha$  for each value of  $n''$ .

Thus the separation of the two systems is largely accounted for by a constant electronic part, but contains also a small variable part which is vibrational in character. A still smaller rotational part (mainly  $\kappa_\beta - \kappa_\alpha$ ) is not definitely excluded, but is probably negligible. The analysis further indicates a common set of initial vibrational states associated, of course, with a common initial electronic state of the molecule for the two systems, and two different sets of final vibrational states associated with two distinct final electronic states, the energy difference of which is represented by the origin separation  $\nu_\beta^e - \nu_\alpha^e = 2360$ . This result is illustrated by means of an energy-level diagram in fig. 1.

From the foregoing analysis it is evident that the moment of inertia of (and therefore also the inter-nuclear distance in) the SnCl molecule is greater in either of the final states than in the initial state. In the first place, this follows from the observed fact that the bands of both systems are degraded towards higher wave-numbers,† even though the bands are un-

\* The coefficients of  $n'$  and  $n''$  have been adjusted to be the same for both equations; the values are a compromise between two pairs which were first obtained, differing slightly for  $\alpha$  and  $\beta$ . The two pairs, however, could be interchanged over the range  $n' = 0$  to  $n' = 4$  without appreciable effect on the resulting values of  $\nu_\alpha$  and  $\nu_\beta$ .

† W. E. Curtis, 'Roy. Soc. Proc.,' A, vol. 101, pp. 40-43 (1922); A. Sommerfeld, 'Atombau und Spektrallinien,' 4th edn., p. 718 *et seq.*



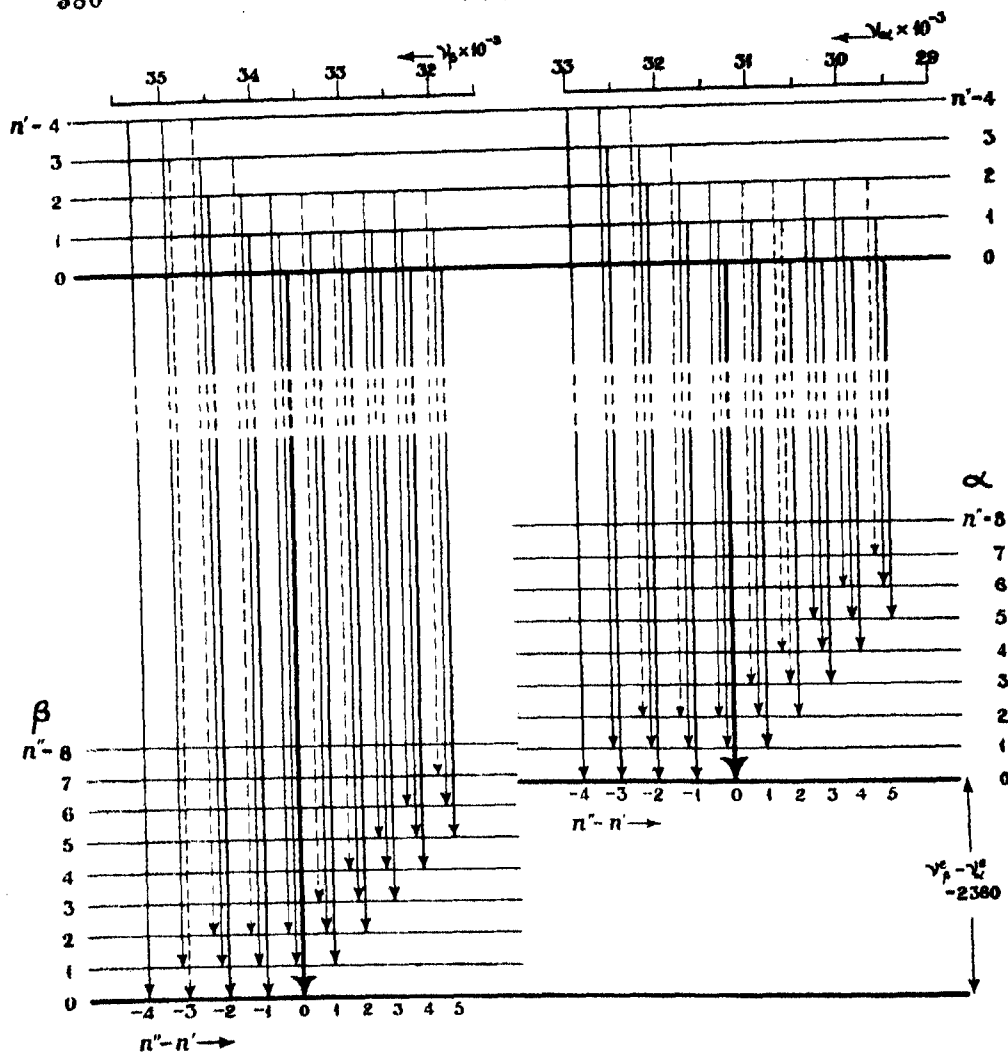


FIG. 1.—Electronic and vibrational energy levels for SnCl. The common initial electronic level and the two final electronic levels for the systems  $\alpha$  and  $\beta$  are denoted by the thick horizontal lines, and the vibrational levels associated with each electronic level by thinner horizontal lines drawn to scale; the scale being indicated by the electronic separation,  $\nu_\beta - \nu_\alpha = 2360$ . The height of the initial set of levels is much reduced; the  $n' = 0$  level would be, on the scale so indicated, about 41 cms. above the level  $n'' = 0$  for system  $\beta$ . The vertical arrows denoting the transitions associated with the emission of the bands, are spaced horizontally on a linear scale of  $\nu$  for each system, i.e., almost as the band-heads to which they pertain occur in a grating spectrogram (cf. Plate 2, strip 4). In order to avoid confusion, the two systems, which actually overlap one another, are entirely separated in the diagram, and their respective sets of final levels are drawn only half-way across the diagram, with the exception of the level  $n'' = 0$  for system  $\beta$ . For the same reason, not more than three bands of any one group are shown. The values of  $n'' - n'$  characterising the groups are given underneath the two  $n' = 0$  levels. The (0, 0) band for each system is represented by a thicker arrow than the rest, and doubtful or unobserved bands by broken-line arrows.

resolved. It follows also from the fact, which can be seen from the equations (10, $\alpha$ ) and (10, $\beta$ ), that the vibrational frequency coefficient ( $a''c$ ,  $a''c$ )\* for either of the final states is less than the coefficient ( $a'c$ ) for the initial state, since Birge and Mecke have found that, as a rule† without a known exception, a decrease of vibrational frequency is correlated with an increase of moment of inertia. The fact that the final vibrational energy coefficients  $a''$ ,  $b''$  in (10, $\beta$ ) are not very different from those in (10, $\alpha$ ) indicates that the difference between the two final electronic states is of such a character as to have very little effect on the inter-atomic forces in the SnCl molecule. If the final electronic state for system  $\beta$  be the normal state of the molecule, that for system  $\alpha$  will presumably be something in the nature of a metastable excited state.‡

#### 6. Isotope Effects.

(i) *The Chlorine Isotope Effect.*—In the early stages of the observations several heads were found which, on the one hand, are incapable of inclusion in the two systems of Table II, and, on the other hand, are not attributable to a source other than that of the bands so included, namely, SnCl. The data for these heads are printed in italics in Table I. Each one, it will be observed, is close to, and on the less refrangible side of, a head of higher intensity—one of the strongest heads of its system in some cases. These additional heads are accounted for by the chlorine isotope effect.§ That is to say, attributing the bands already classified in Table II to the monochloride containing the lighter and more abundant isotope of chlorine, SnCl<sup>35</sup>, the bands not classified in

\* See footnote, p. 374.

† See rule and footnote on p. 376.

‡ In this connection Dr. Mulliken has pointed out, in a letter to the author, that the electronic separation 2360 in SnCl is of the same order of magnitude as the doublet separation,  $1\pi_2 - 1\pi_1 = 2213$ , in the line spectrum of In, the element preceding Sn and having the same extra-nuclear structure as Sn<sup>+</sup>. For In the term  $1\pi_2$  represents the normal state of the atom, and the term  $1\pi_1$  a metastable excited state. (See A. Fowler, "Report on Series in Line Spectra," 'Phys. Soc. Lond.,' 1922, p. 159, for notation and In data.) In view of the relations which have recently been noted between the electronic separations in the band systems of the alkaline-earth halides and the doublet separations of the preceding alkali metals (R. S. Mulliken, III, pp. 31 and 32; and R. Mecke, 'Die Naturwissenschaften,' vol. 36, p. 755 (September 4, 1925)), the above comparison between SnCl and In may acquire significance when further observations of the spectra of the halides of group IV elements are made.

§ The writer is indebted to Dr. Mulliken for very valuable help in the analysis. In the course of a discussion, which involved an examination of the photographs and data, he recognized the isotope effect and generously placed his knowledge of the subject at the writer's disposal.

Table II are to be attributed to  $\text{SnCl}^{37}$ , containing the heavier and less abundant isotope.

Mulliken\* has discussed the general theory, and carried out investigations of several examples, of the isotope effect in electronic band spectra. Consider a mixture containing two isotopic molecules whose masses are  $M_1 + M'$  and  $M_2 + M'$ , where  $M_1$  and  $M_2$  are respectively the mass-numbers of the more abundant and the less abundant isotopes of one element, and  $M'$  is that of the second element, which is in the simplest case "non-isotopic." The isotope effect is measured by the displacement or difference between the wave-number  $\nu_1$  of a band-line due to the more abundant molecule  $M_1M'$ , and the wave-number  $\nu_2$  of an identically numbered line due to the less abundant molecule  $M_2M'$ .

In accordance with equations (3) the total isotope effect is considered as the sum of three separate effects: the electronic, the vibrational, and the rotational isotope effects; i.e.,

$$\nu_2 - \nu_1 = (\nu_2^e - \nu_1^e) + (\nu_2^v - \nu_1^v) + (\nu_2^m - \nu_1^m). \quad (12)$$

The electronic isotope effect  $(\nu_2^e - \nu_1^e)$  is negligibly small, so that corresponding band systems of the two molecules have a common system-origin ( $\nu^e$ ). At the *origin of a band*, ( $\nu^m = 0$ ), the observed isotope effect is vibrational only, while at any other point, e.g., the *head*, of a band it has a small rotational part which, Mulliken shows, is represented approximately by

$$\nu_2^m - \nu_1^m = 2(\rho - 1)\nu_1^m, \quad (13)$$

where  $\nu^m$  is the separation between that point and the origin of the same band, and

$$\rho = \sqrt{\frac{1/M_2 + 1/M'}{1/M_1 + 1/M'}}, \text{ and hence approximately } \rho - 1 = \frac{M'(M_1 - M_2)}{2M_2(M_1 + M')}. \quad (14)$$

In cases such as the present one of  $\text{SnCl}$ , in which the bands are unresolved, this rotational effect may be neglected; the error so introduced being within the limits of error in the measurement of the unresolved head. Only the vibrational isotope displacement has then to be taken into account, just as if the *origins* and not the *heads* were measured. For the observed *total* isotope displacement  $\nu_2 - \nu_1$  at the  $\text{SnCl}$  heads we may, then, substitute the

\* *Loc. cit.*, I, Theory; II, BO; III, CuI; IV, SiN.

approximate expression\* which Mulliken gives for the vibrational displacement, namely

$$\nu_2'' - \nu_1'' = (\rho - 1) \nu_1'', \quad (15)$$

where  $\nu_1''$  for any  $\text{SnCl}^{35}$  head may be taken as its separation from the head of the (0, 0) band of the same system, though it is strictly the separation from the origin of the (0, 0) band.

In the case of chlorine, since  $\text{Cl}^{35}$  is the more abundant isotope,  $M_1 = 35$  and  $M_2 = 37$ , and the isotope coefficient  $\rho - 1$  is negative. The displacement  $\nu_2 - \nu_1$  is, therefore, negative on the more refrangible side of the (0, 0) head ( $\nu_1''$  positive), and positive on the less refrangible side. That is to say, the system of weaker bands due to the less abundant heavier molecule  $\text{SnCl}^{37}$  is similar to that of  $\text{SnCl}^{35}$ , but on a smaller scale. A little consideration shows that a favourable  $\text{SnCl}^{35}$  band to exhibit the effect will, therefore, be one that is (i) fairly strong since the  $\text{SnCl}^{37}$  band may be expected to have only about one-third the intensity of the corresponding  $\text{SnCl}^{35}$  band; (ii) degraded away from the corresponding  $\text{SnCl}^{37}$  band, i.e., a band on the more refrangible side of the (0, 0) band of the same system, and (iii) not confused by the structure by preceding bands of the same group (see p. 376). Reference to Table II indicates (1, 0), (2, 0), (3, 0) and (2, 2) as the bands which fulfil these conditions, and (3, 1) as a possible but less favourable band, for isotope observations.

Before the Cl isotope displacement can be finally calculated we require to know the mass  $M'$  of the other atom of the molecule, i.e., of the Sn atom. Aston† has shown that tin contains seven (or possibly eight) isotopes, the mass-numbers of which in order of diminishing abundance are 120, 118, 116, 124, 119, 117, 122 and (121). While, as will be seen later, it is possible to trace a tin isotope effect, for the purpose of calculating the chlorine isotope effect we may take either the mean mass, as given by the chemical atomic weight, or the mass of the most abundant isotope, i.e., 118.7 or 120, since from formula (14) it is obvious that a small variation of  $M'$  will not appreciably affect the value of the isotope coefficient, itself small. For either value of  $M'$  the Cl coefficient is  $\rho - 1 = -0.0209$ , and the displacement  $\nu_2 - \nu_1 = -0.0209 \nu_1''$ ; that is, the  $\text{Sn}^{120}\text{Cl}^{37}$  head is 2.09 per cent. nearer to the (0, 0) head than is the

\* This expression holds strictly only if the coefficients of  $n'^2$  and  $n''^2$  are zero. But they are so small in the present case, and the observed displacements  $\nu_2 - \nu_1$  so relatively few and inaccurate, that the expression is sufficiently exact. It would not suffice for such a case as Mulliken's  $\text{B}^{16}\text{O} - \text{B}^{17}\text{O}$ .

† F. W. Aston, 'Isotopes,' Second Edition (1924), p. 31.

corresponding  $\text{Sn}^{120}\text{Cl}^{35}$  head. A comparison of the observed and calculated Cl isotope displacements in each of the systems  $\alpha$  and  $\beta$  is shown in Table IV.

Table IV. — Chlorine Isotope Effect.

Isotope displacement,  $\nu_2 - \nu_1 = -0.0209 \nu_1''$ .

System.	$n'$	$n''$	SnCl <sup>35</sup> head.		SnCl <sup>37</sup> head.		Cl Isotope displacement.	
			$\nu_1$ obs.	Int.	$\nu_1''$ obs.	$\nu_2$ obs.	Int.	Obs. = $\nu_2 - \nu_1$ . Calc. = $-0.0209 \nu_1''$ .
$\alpha$	0	0	31282					
	1	0	31692	7	430	31684	2	— 9
	2	0	32120	5	858	32103	2	— 17
	3	0	32547	1	1285	32520	0	— 27
	2	2	31419	3	157	31416	0?	— 3
	3	1	32197	4	935	32171*	0?	— 26
$\beta$	0	0	33622					
	1	0	34052	10	430	34042	3	— 10
	2	0	34480	7	858	34464	2	— 16
	3	0	[34905.7]†	—	1285	34884	2	— 21.7
	2	2	33782	5	157	33779	2	— 3
	3	1	34556	5	935	34532	2?	— 24

\* An alternative interpretation is SnCl<sup>35</sup>  $\beta$  (3, 8) (see Table II $\beta$ ).

† Masked by Sn  $\lambda$  2863.320,  $\nu$  34914.3.  $\nu_{\text{calc}}$  from formula 8 ( $\beta$ ) inserted.

The comparison between the theoretical and observed Cl isotope effects may be made in another way. Mulliken has shown that if the coefficients of  $n'$ ,  $n'^2$ ,  $n''$ ,  $n''^2$  in the expression (equation 5) for  $\nu''$  be  $a_1'$ ,  $b_1'$ ,  $a_1''$ ,  $b_1''$  respectively for the more abundant, and  $a_2'$ ,  $b_2'$ ,  $a_2''$ ,  $b_2''$  respectively for the less abundant isotope, then the ratios of the coefficients of corresponding terms are

$$a_2'/a_1' = a_2''/a_1'' = \rho \quad \text{and} \quad b_2'/b_1' = b_2''/b_1'' = \rho^2.$$

Hence, representing the SnCl<sup>35</sup> heads, of each system in turn, approximately by (cf. equations 8):—

$$\nu_1 = (\nu^0 + \kappa_1) + (a_1'n' - b_1'n'^2) - (a_1''n'' - b_1''n''^2), \quad (8_1)$$

the SnCl<sup>37</sup> heads will be given approximately by:—

$$\nu_2 = (\nu^0 + \kappa_2) + (\rho a_1'n' - \rho^2 b_1'n'^2) - (\rho a_1''n'' - \rho^2 b_1''n''^2). \quad (8_2)$$

$\kappa_2 - \kappa_1$  is the main part (constant from band to band) of the rotational isotope effect at the head of each band, including the (0, 0) band, and is certainly too

small to be taken into account in the present observations : we may, therefore, assume  $\kappa_2 = \kappa_1 = \kappa$ .

From the formulæ ( $10_1 \alpha$  and  $10_1 \beta$ ) approximately representing the observations of the  $\text{SnCl}^{35}$  heads, and the theoretical values of the Cl isotope coefficients,  $\rho = 1 - 0.0209 = 0.9791$  and  $\rho^2 = 0.9586$ , the following approximate formulæ for the  $\text{SnCl}^{37}$  heads are derived :—

$$\nu_{2a} = 31262.5 + 422.3 n' - 1.15 n'^2 - 346.1 n'' + 0.96 n''^2, \quad (10_2 \alpha)$$

$$\nu_{2\beta} = 33622.6 + 422.3 n' - 1.15 n'^2 - 344.1 n'' + 1.15 n''^2. \quad (10_2 \beta)$$

The residuals are shown in italics in the  $\nu_{\text{obs.}} - \nu_{\text{calc.}}$  column of Table I.

In spite of the small number of  $\text{SnCl}^{37}$  bands observed the roughly quantitative agreement shown, both here and in Table IV, affords considerable support for the deduction that the emitter of both systems is  $\text{SnCl}$  (with the further attribution of the bands in Table II to  $\text{SnCl}^{35}$  and of the additional bands to  $\text{SnCl}^{37}$ ), and for the assumption as to the location of the origin of each system. It certainly indicates that the true system-origin must be very near the band which has been called (0, 0), and must lie in the group  $n'' - n' = 0$ . The agreement is not sufficiently quantitative, however, to exclude the possibility that the true origin may be at  $(-\frac{1}{2}, -\frac{1}{2})$  on our numeration (in which case the correct numeration would begin with  $(\frac{1}{2}, \frac{1}{2})$  instead of (0, 0) for the first observed band) since the calculated values of the isotope displacement,  $\nu_2 - \nu_1$ , would be increased only by about  $0.8 \text{ cm.}^{-1}$  if the values of  $n'$  and  $n''$  were each increased by  $\frac{1}{2}$ . In the absence of direct evidence for  $(\frac{1}{2}, \frac{1}{2})$  it is best to assign (0, 0) to the first band of the group  $n'' - n' = 0$ , as has already been done.

(ii) *The Tin Isotope Effect.*—Taking the seven certain Sn isotopes we should expect theoretically seven different positions of the band-head corresponding to  $\text{Cl}^{36}$ , and a further seven corresponding to  $\text{Cl}^{37}$ . The Sn isotope effect can readily be shown to be of a much smaller order of magnitude than the foregoing Cl isotope effect. It has already been pointed out that the magnitude of the Cl isotope displacement is, to a first order, independent of the Sn mass selected. Similarly, in calculating the Sn isotope displacement, to a first order, it is immaterial what Cl mass is selected. Putting  $M' = 35$ , the mass-number of the more abundant Cl isotope ;  $M_1 = 120$ , that of the most abundant Sn isotope ; and  $M_2 =$  each of the other Sn mass-numbers in turn, we have from the approximate formula (14) the following coefficients for the respective displacements of the heads of  $\text{Sn}^{116}\text{Cl}^{35}$ , etc., from the corresponding  $\text{Sn}^{120}\text{Cl}^{35}$  head —

$$\begin{array}{ccccccc} M_2 : - & 116 & 117 & 118 & 119 & (121) & 122 & 124 \\ (p-1) : - & +.00389 & +.00289 & +.00191 & +.00095 & (-.00093) & -.00185 & -.00364 \end{array}$$

The extreme Sn displacement ( $\cdot 0075 \nu_1''$ ) is thus rather more than one-third of the Cl displacement ( $\cdot 0209 \nu_1''$ ).

Similarly, when  $M' = 37$ , the coefficients for the respective displacements of  $\text{Sn}^{116}\text{Cl}^{37}$ , etc. from  $\text{Sn}^{120}\text{Cl}^{37}$  are:—

$$M_2:— \quad 116 \quad 117 \quad 118 \quad 119 \quad (121) \quad 122 \quad 124$$

$$(\rho-1):— +\cdot 00406 +\cdot 00302 +00200 +\cdot 00099 (-\cdot 00097) -\cdot 00193 -\cdot 00380.$$

These are 4 per cent. greater than for  $M' = 35$ ; but  $\nu''$ , the separation from (0, 0), is 2 per cent. less for  $\text{Sn}^{120}\text{Cl}^{37}$  than for  $\text{Sn}^{120}\text{Cl}^{35}$  (see Cl isotope effect); hence the Sn isotope *displacements*  $(\rho-1)\nu''$  will be only about 2 per cent. greater for  $\text{SnCl}^{37}$  than for  $\text{SnCl}^{35}$ ,—a difference which we can disregard entirely.

For a band on the high wave-number side of (0, 0), *e.g.*,—the (2, 0) band, the complete scheme is indicated in fig. 2 where the relative intensities are represented by the heights, and wave-numbers are shown horizontally.

Actually, what is observed under the relatively low resolution employed is only a broadening or diffuseness of certain heads of  $\text{SnCl}^{35}$  and  $\text{SnCl}^{37}$ . This character, which was evident from the earliest stages of the grating observations, certainly appears to be responsible for the somewhat wide limits of observational errors. Under somewhat higher resolution each favourable band of  $\text{SnCl}^{35}$  would be expected to appear double, one component, due to  $\text{Sn}^{124}\text{Cl}^{35}$ , being weak, and the other, an unresolved blend of heads of  $\text{Sn}^{116-122}\text{Cl}^{35}$ , being stronger but broad and diffuse; and similarly for the corresponding  $\text{SnCl}^{37}$  band. In the case of one band, namely (2, 0) of system  $\beta$ , this duplicity was observed in one of the grating plates; the  $\text{SnCl}^{35}$  head was measured as a doublet on every occasion, and it was suspected that the  $\text{SnCl}^{37}$  head was also on the point of resolution. The estimated separation was of the order one-sixth to one-eighth of the Cl isotope displacement. Observations of the  $\text{SnCl}_4$  discharge as used in the present work, under resolving power high enough for a verification of the complete isotope effect shown in fig. 2, do not seem feasible.

### 7. The Less Refrangible Bands.

The bands in the less refrangible region ( $\lambda$  3486— $\lambda$  3910) occur mainly in groups of comparatively close bands, four of which groups have been detected. The most prominent of the groups is the one of shortest wave-lengths, in which at least two heads near  $\lambda$  3487 and  $\lambda$  3494 are strong doublets, the former being the stronger and more widely separated. In each doublet the shorter wave component is the weaker and less band-like in appearance; in fact, a little doubt

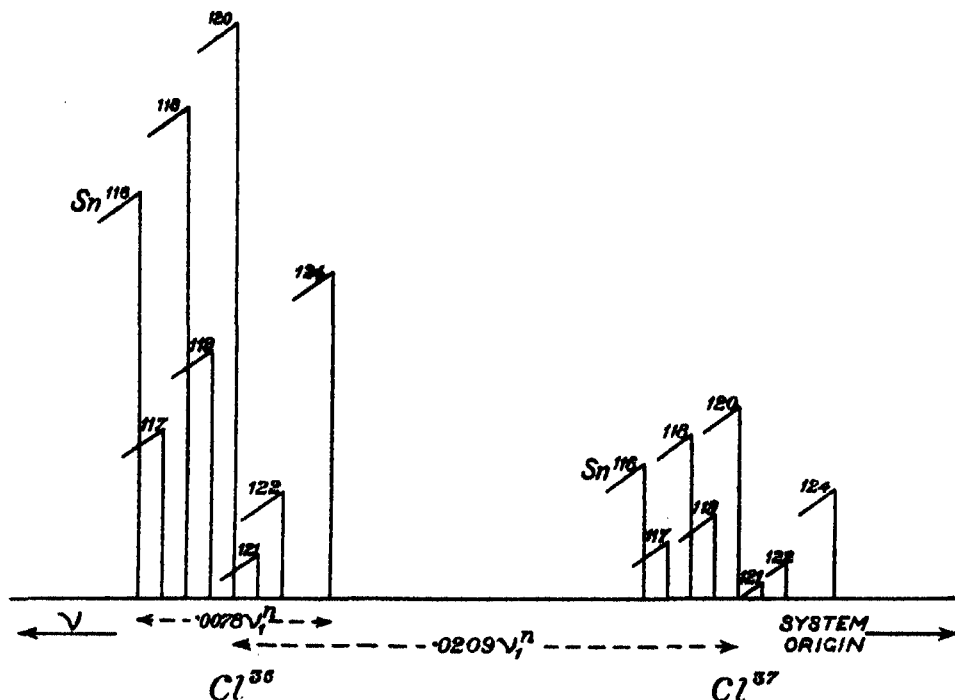


FIG. 2.—Calculated vibrational isotope effects of Sn and Cl in a SnCl band on the high wave-number side of the system-origin. Relative intensities are roughly represented by heights, and isotope displacements of heads having a given pair of values of  $n'$ ,  $n''$  are shown horizontally on a linear scale of  $\nu$ . The oblique lines indicate that the bands are degraded towards the higher wave-numbers. If the diagram represent the (2, 0) band, the (3, 0) would fall about 161 cms. to the left of the diagram, and would resemble the (2, 0) pattern increased to  $3/2$  of its width and very much diminished in height. A similar pattern about the same distance to the right of the diagram, compressed to  $1/2$  of its width and increased in height would represent the (1, 0) band. In (0, 0) this pattern would approximately coalesce into a single strong band about 322 cms. to the right of the diagram. The patterns for (0, 1), (0, 2), etc., would be still further to the right, and consist of lateral reversals of the above with, of course, different heights and widths; the oblique lines, however, remaining as shown, to the left downwards.

was felt as to whether these components were lines or band-heads. They have not, however, been identified with known lines, and are therefore included with the other components in Table V. These features of the group are apparent both from the photograph (Plate 2, strips 2a and 2b), and from the table. The small doublet separations decrease in a manner suggesting a constant second difference. The four well observed stronger component-heads form a progression in which the first differences of wave-number increase, and a constant second difference is suggested.



Table V.—Heads of the Less Refrangible Bands of Tin Chloride.  
(Degraded towards the red.)

$\lambda_{\text{air}}$ (l.A.).	Int.	$\nu_{\text{vac}}$ (cm. <sup>-1</sup> ).	$\Delta_1\nu$ .	$\lambda_{\text{air}}$ (l.A.).	Int.	$\nu_{\text{vac}}$ (cm. <sup>-1</sup> ).	$\Delta_1\nu$ .
3486.2 3487.8	5l 10	28676 28663	> 13	3808.2	1	26252	
3493.7 3494.7	3l 8	28615 28607	> 8	3826.4	4l	26127	68
3502.0 3502.6	? 1n 2	28547 28543	> 4	3836.4	4	26059	73
3511.2	1	28472		3847.1	4	25986	
3758.6	10	26598		3877.3	1	25784	67
3767.3	8	26537		3887.4	3	25717	72
3776.6	5	26471		3898.3	3	25645	77
3786.3	2	26404		3910.0	1	25548	

$n$  = nebulous,  $l$  = line-like, ? = doubtful.

The remaining bands, unlike those of the above group, have single heads. Generally speaking, however, a similar progression is fragmentarily indicated in each group. The second group (Plate 2, strips 3a and 3b) beginning at  $\lambda$  3759 shows a rapid decrease in intensity, as does the first group, but the first differences are irregular; the unsatisfactory observation of the fourth head is probably responsible.

Since these less refrangible chloride bands have the region  $\lambda$  3486 to  $\lambda$  3910 in common with the oxide bands, which also degrade to the red, a comparison of data was made in order to remove any doubt as to their independence; this appeared to be the more necessary as one of the strongest tin oxide heads in Eder and Valenta's photographs is that for which these investigators gave  $\lambda$  3487, and von der Seipen  $\lambda$  3485, and is very near one of the two strong chloride bands of the present set. Such close proximity of oxide and chloride heads, however, never recurs. Moreover all other strong oxide heads are definitely absent in the  $\text{SnCl}_4$  plates.

Too little is known of these bands to say whether they are emitted by a polyatomic tin chloride, or by the same molecule ( $\text{SnCl}$ ) as are the Systems  $\alpha$  and  $\beta$ . In the latter event it would appear that they constitute one or more incompletely developed systems, in which  $n'$  and  $n''$  for the observed bands are too small to give detectable isotope effects. The group near  $\lambda 3487$  may belong to an entirely different system from the rest, perhaps a system with  $n''-n'$  confined to a single value, say unity. While these results do not go far towards complete analysis of the less refrangible set of bands it seemed worth while, in the absence of any previously recorded measurements of the spectrum, to add this brief account.

#### 8. Summary.

1. The spectrum of the uncondensed discharge through  $\text{SnCl}_4$  vapour comprises, in addition to Sn and Cl lines, a continuous spectrum in the visible region between  $\lambda 4900$  and  $\lambda 3950$ , and a hitherto unrecorded band spectrum in the near ultra-violet. The bands belong to two distinct sets occupying the regions  $\lambda 3910-\lambda 3486$  and  $\lambda 3405-\lambda 2830$  respectively. The band heads have been measured in the first order of a grating spectrograph. None of the bands has been resolved into lines. Each set is attributed to a chloride of tin.

2. The bands in the more refrangible set constitute two systems,  $\alpha$  and  $\beta$ , of the normal Deslandres type. The systems closely resemble one another, (a) in their ranges of values of the initial and final vibrational quantum numbers,  $n'$ ,  $n''$ ;  $n'$  in each system ranging from 0 to 4 or 5, and  $n''$  from 0 to 8 or 9; (b) in the intensities of like-numbered bands, and in their intensity distribution which is of a fairly normal type; (c) in their progressions of first differences of wave-numbers, and therefore in their vibrational energy coefficients; and (d) in consisting of bands which degrade towards the further ultra-violet, indicating that the moment of inertia of the molecule which emits  $\alpha$  and  $\beta$  is greater in the final state than in the initial state, in the case of each system.

3. The separation ( $\nu_\beta - \nu_\alpha$ ) of like-numbered bands in  $\alpha$  and  $\beta$  increases appreciably with  $n''$ , while it is independent of  $n'$ . Thus the inter-system separation is largely accounted for by an electronic term (viz., the separation of the origins of systems  $\alpha$  and  $\beta$ ), but contains also a vibrational term dependent only on  $n''$ . This indicates a common initial electronic state (with its associated vibrational states) and two distinct final electronic states (each with its associated vibrational states) for the two systems. The two ( $\alpha$  and  $\beta$ ) final electronic states of the molecule are not very different as regards vibrational energies and, therefore, inter-atomic forces.

4. If systems  $\alpha$  and  $\beta$  be ascribed to  $\text{SnCl}^{35}$ , a few additional bands in the same region are attributable to  $\text{SnCl}^{37}$ , in accordance with Mulliken's theoretical formulæ for the vibrational isotope effect. This Cl isotope effect affords considerable support for the above assignment of  $n'$ ,  $n''$  in each system. There is also some indication of the Sn isotope effect, which is smaller and more complicated, and accounts for the observed diffuseness of most of the band heads in both systems.

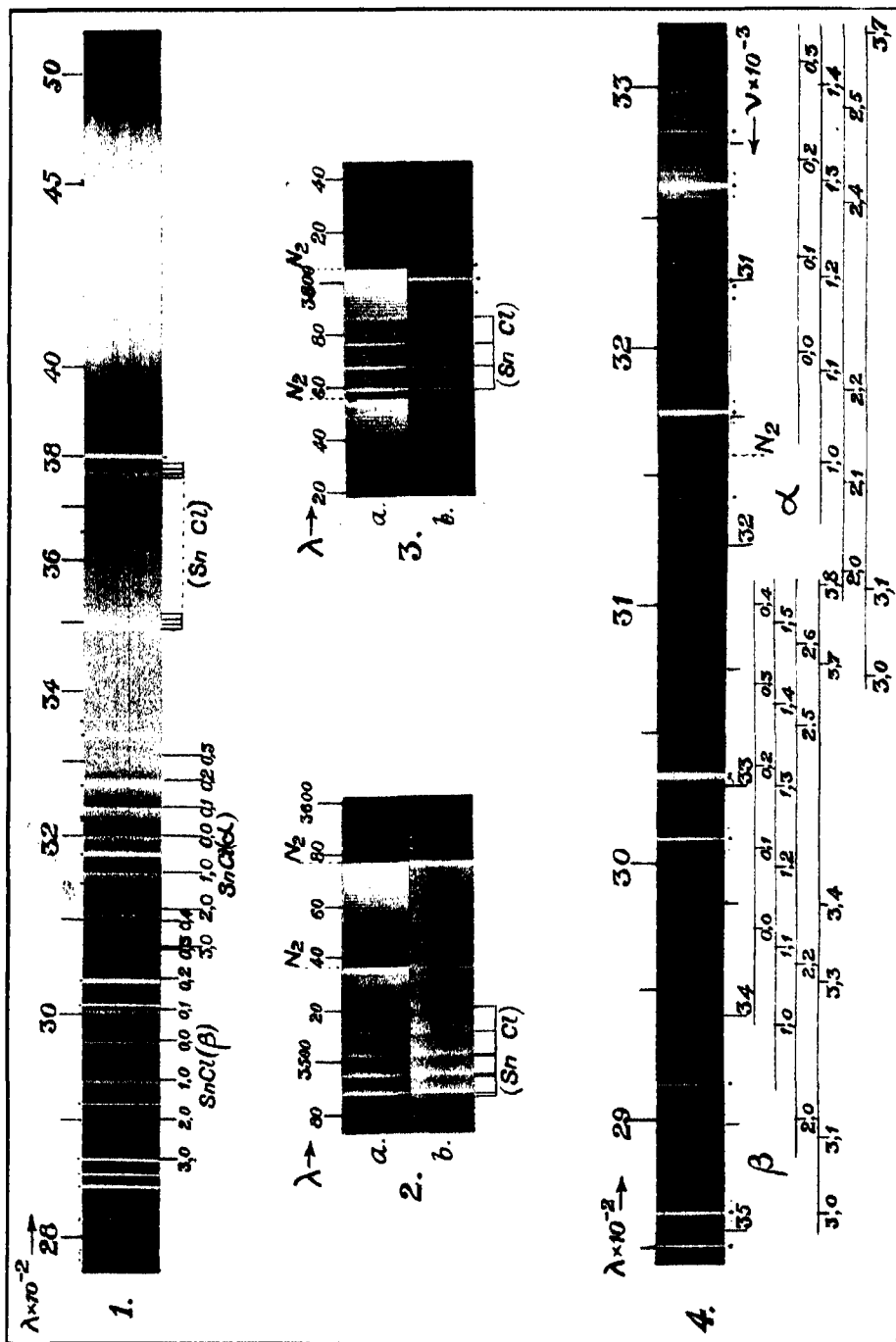
5. The less refrangible set consists of several groups, each containing a few close bands degraded towards the red. The first differences between the wave-numbers of the band heads in each group are of the same order from group to group. Too little is known of these bands to say whether they are emitted by  $\text{SnCl}$ , as are systems  $\alpha$  and  $\beta$ , or by a polyatomic chloride.

The cost of the Hilger micrometer used in this investigation was defrayed by a grant from the Government Grants Committee of the Royal Society. The author's best thanks are again due to Prof. Andrade for affording every facility for spectroscopic work in the Artillery College, and for his interest in, and revision of, the paper. The author is greatly indebted to Dr. R. S. Mulliken for very valuable help already acknowledged.

#### DESCRIPTION OF PLATE 2.

$\text{SnCl}_4$  uncondensed discharge :—

1. Hilger E6 quartz spectrograph ( $\times 6.8$ ). Continuous spectrum in visible region; the first two groups ( $\lambda\lambda$  3487, 3759) of the less refrangible bands of tin chloride; and systems  $\alpha$  and  $\beta$  of the more refrangible bands of tin chloride ( $\text{SnCl}^{35}$ ).
  - 2a, 2b and 3a, 3b.—Concave grating spectrograph ( $\times 2.6$ ). Groups of the less refrangible bands near  $\lambda$  3487 and  $\lambda$  3759 respectively. The  $\text{N}_2$  second positive bands are very strong in the upper strip (a) in each case, and of moderate intensity in the lower strip (b).
  4. Concave grating spectrograph ( $\times 2.6$ ). More refrangible ( $\text{SnCl}^{35}$ ) bands, systems  $\alpha$  and  $\beta$ . The  $\text{SnCl}^{37}$  heads (2, 0) and (1, 0) were visible in the enlargement of which the plate is a reproduction.
- Sn lines and ghosts are indicated by dots.
-



Band Spectrum of Tin Monochloride.



*Some Physical Properties of Steel and their Determination.*

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The work described in the present paper was performed with the primary object of investigating the constitution of steel by new methods. The development and perfection of these methods, and the standardization of the relevant experimental conditions were, at the outset, looked upon as purely incidental. During the course of the work, however, it became apparent that this secondary object was of as much importance as the results originally sought, and in consequence considerable care and attention were given to it. The paper is divided into three sections:—Electrode Potential, Electrical Resistance, and Change of Resistance during Tempering.

*Heat-Treatment.*

All heat-treatment was carried out in a wire-wound electric resistance furnace. The specimens were heated in a transparent silica tube, which was capable of being evacuated by means of a Toepler mercury pump. No difficulty was found in maintaining the vacuum even at the highest temperatures used.

Except where otherwise stated, the annealed specimens were soaked for one hour at the annealing temperature, and allowed to cool very slowly in the furnace. After this treatment they were generally found to be quite untarnished. In a few cases they were slightly heat-tinted.

The specimens for quenching were heated in a porcelain boat, to one end of which a wire was attached. When they were ready for quenching, the vacuum was broken, the stopper removed, and by means of the attached wire the boat was drawn into a large volume of iced brine. The transference of the specimens from the furnace to the quenching bath occupied less than one second.

Temperatures were measured by means of platinum/platinum-iridium thermocouples, and a Siemens' direct-reading galvanometer. The couples were standardized from time to time against known melting points.

*Electrode Potential.*

The investigation of the electrode potential of steel is rendered difficult because of the complexity of the material which causes local electrolytic actions between the various constituents.

Herschkowitz (1) found that electrodes composed of two or more metals could be classified under three headings :

Class I.—The metals form a mechanical mixture. The potential is that of the most active metal.

It has been shown that in a metal that exists in more than one allotropic form, each allotrope has its own distinct electrode potential. Thus, alpha and gamma iron would be expected to give different values, but if these modifications are mutually insoluble, the potential of a mixture of the two would be that of the more active form.

Class II.—The metals form a solid solution. The latter is always less active than the most active component. In this class, the concentration-potential curve has a logarithmic form.

Class III.—An intermetallic compound is formed. If the compound can exist in the solution as such, it has its own solution pressure. On the concentration-potential curve, intermetallic compounds are indicated by discontinuities.

It has been shown by Reinders (2) who examined the relation between the composition of an alloy and that of the electrolyte with which it is in equilibrium, that except in the cases where the components of the alloy have widely different potentials, a complex electrolyte is theoretically necessary. The provision of such an electrolyte has been found to present great practical difficulties, and in the case of steel it does not appear to be possible to provide an electrolyte with which the specimen would be in equilibrium. In the present investigation it was found that satisfactory results could be obtained with a solution of an iron salt.

*Method of Measurement Employed.*—The method adopted was that of using two half-cells, one containing the specimen dipping into the electrolyte, the other being a normal calomel cell, connected together by means of a normal solution of potassium chloride. The potential difference between the two electrodes was determined by means of a potentiometer, which gave readings with an accuracy of 0.1 microvolt.

The International Congress at Berlin (3) recommended that directly-measured values should in all cases be given, the auxiliary electrode being a normal calomel cell. This method of stating the results has been followed in the present investigation, the values given being the E.M.F. of the combination steel/electrolyte/normal KCl/calomel electrode, as read by the potentiometer.

*Experimental.*—The composition of the steels is given in Table I, and the method of heat-treatment has been described. The specimens used were in

the form of cylinders  $\frac{3}{4}$  inch in length and  $\frac{1}{4}$  inch in diameter, with a hole at one end into which fitted a tapered rod which supported the specimen inside the cell, and acted as the current conductor. The rod was fitted with a piece of thick tight-fitting rubber tubing, which acted as a stopper in the mouth of the half-cell.

Two differently treated carbon steels were first experimented with, and many attempts were made to obtain definite results, capable of repetition. Electrode potential being a surface effect, it was obvious that a clean surface for the specimen was necessary, and all surfaces were cleaned with emery before immersion in the electrolyte.

In the first attempt the bare electrodes were partly immersed in normal ferric chloride solution, and the potential was read off on the potentiometer. It was found that the potential altered steadily, falling in half an hour to a minimum from which it increased gradually without attaining a constant value even after four hours. It is the custom amongst investigators to read the potential after a considerable time-interval when the value has attained constancy, and to consider this as the value for the alloy. In the present case no such constant value was obtained.

After repeated attempts with different electrolytes of various concentrations and with varying conditions, it was found that consistent results could only be obtained by observing the following conditions :—

(a) In the preparation of the surface exposed to the electrolyte, great care had to be taken. As the preparation of the sides of the specimens was difficult, it was found advantageous to insulate them from the electrolyte. For this purpose shellac varnish was found satisfactory.

(b) The ends of the specimens which were exposed to the electrolyte were carefully surfaced by means of 000 emery paper.

(c) Each measurement of the electrode potential was repeated many times. A fresh surface was prepared each time.

The procedure finally adopted was as follows :—

The heat-treated specimen was carefully cleaned with emery paper and fixed to a connecting rod. The end was then surfaced and the sides varnished. When the varnish was dry the specimen was immersed in the electrolyte, which together with the calomel cell and the connecting link of potassium chloride solution was kept at 18° C., by means of a simple thermostat. Fifteen seconds after immersion of the specimen in the liquid, the circuit was made by depressing the potentiometer key, and an approximate reading of the potential was taken. The specimen was then cleaned, polished,



varnished, dried and again immersed, the potentiometer being set at the value obtained in the first experiment. If any movement of the spot of light was noted, the potentiometer was reset, and the operations repeated until, on depressing the key, no movement of the spot was observed. This was regarded as being the correct value.

#### *Consideration of Results.*

As far as the authors are aware, no systematic research on the electrode potential of steel has been published. For this reason, it may be advisable to discuss the general meaning of the results before passing on to a detailed consideration of the curves.

The authors consider that in all the steels, annealed or quenched, the values of electrode potential obtained are those of alpha iron modified by the presence of varying amounts of carbon, nickel, and chromium, in solution.

The curves for quenched steels show that the electrode potential decreases as the carbon content increases. This means that the electrode potential of iron is lowered by solution of carbon in it—that is, that iron is rendered less active by dissolved carbon.

As was pointed out in the introduction, the electrode potential of a quenched steel that contains both austenite and martensite must be that of the more active form. From consideration of all their results, the authors have concluded that austenite is much less active than martensite; in quenched steels, therefore, the electrode potential is that of the martensite, and is not influenced by the presence of austenite. Similarly, if in any quenched steel the carbon is not homogeneously distributed through the martensite, the electrode potential must be that of the least concentrated area of martensite exposed to the electrolyte.

*Quenched Steels.*—From figs. 1 and 2 it will be seen that the electrode potential of quenched hypoeutectoid steels is raised by raising the quenching temperature. This means that with increase in quenching temperature the least concentrated area of the solid solution becomes less concentrated in carbon. This accords with the suggestion by Andrew and Hay (4) that carbide segregation occurs on soaking at a temperature above  $A_{c_3}$ .

An increase in quenching temperature lowers the electrode potential of hyper-eutectoid steels, showing that in these steels the concentration of carbon in solution increases with rising quenching temperature—a conclusion that is in agreement with the iron-carbon diagram. The marked deviation of the curve for hypereutectoid steels quenched at  $1100^{\circ}\text{C}$ . from that of the same

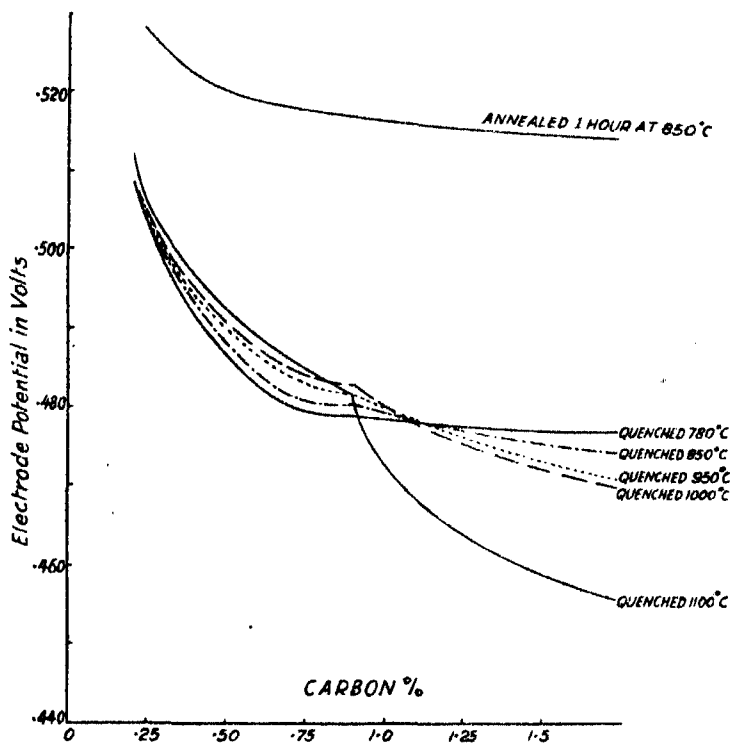


FIG. 1.—Electrode Potential of Carbon Steels.

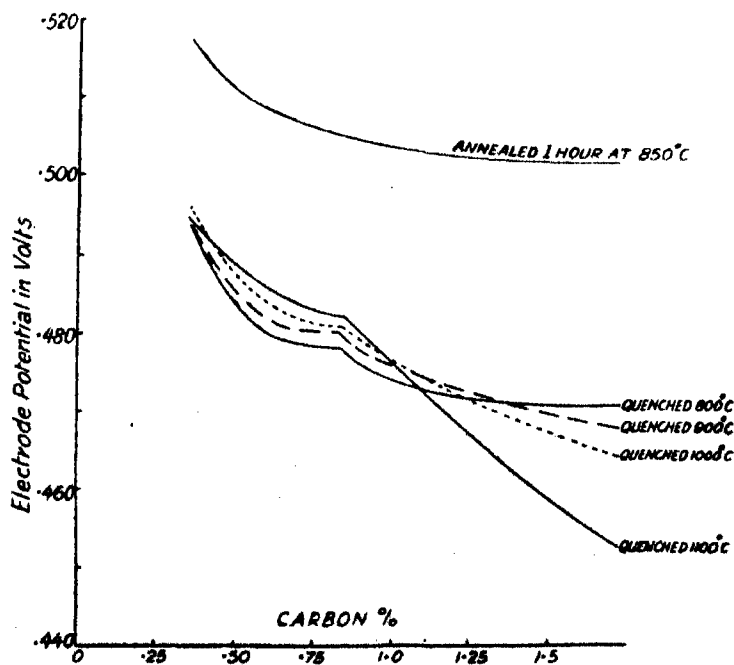


FIG. 2.—Electrode Potential of Chromium Steels.

steels quenched at 1000° C. appears to require comment. When the carbon content is greater than 1.2 per cent., steels quenched at 1100° C. contain austenite; but, as this constituent appears to be less active than martensite, it should not affect the results directly. The curves show that the martensite obtained by quenching high-carbon steels from 1100° C. is much more concentrated than that obtained by quenching from 1000° C.—the difference being greater than would be deduced from the iron-carbon diagram. Two explanations of this anomaly may be advanced: (a) that the cementite line of the diagram is more strongly curved than is generally believed, so that the solubility of carbon in gamma iron at 1100° C. is much greater than at 1000° C. (electrical resistance measurements, however, indicate that this is improbable); or (b) that so long as particles of cementite in hypereutectoid steels remain undissolved before quenching, they may act as nuclei and cause partial precipitation of carbide, even with rapid cooling.

Many observers have noted that a quenched steel evolves heat at room temperature. The heat evolution has been measured by Hadfield (5) and others. As the change undergone should be measurable by other means, it was decided to compare the values of electrode potential measured immediately after quenching with those obtained after allowing the specimens to remain at room temperature for a period of time. Fig. 4A shows that the electrode potential decreased with time. This may be due to the removal of the strain caused by quenching.

Two series of carbon steels, quenched at 1100° C. and 780° C. respectively, and a series of chromium steels, quenched at 1100° C., were immersed in liquid air for one hour, the electrode potential at 18° C. being measured before and after immersion. No appreciable change in electrode potential was observed. This indicates that martensite, unlike austenite, is not affected by liquid air.

*Tempered Steels.*—The effect of tempering is shown in figs. 3 and 4, in which are given the curves for carbon and chromium steels respectively. The specimens were quenched at 1100° C. and tempered successively for 3 hours at the temperatures indicated.

From the curves it is seen that when the tempering temperature is raised the electrode-potential curves rise progressively, showing that the amount of carbon in solution is reduced by tempering. An approximate estimate of the amount of carbon remaining in solution in any steel after tempering at the temperatures shown, can be obtained by drawing a horizontal line from the point representing the steel on the appropriate tempering curve, to cut the curve of the quenched steels. For example, a horizontal line drawn from the

point representing 1 per cent. of carbon on the 350° C. curve will cut the "quenched curve" at a point corresponding to about 0.27 per cent. of carbon, indicating that after tempering for 3 hours at 350° C. a 1 per cent. carbon steel will still contain 0.27 per cent. of carbon in solution.

It is apparent from the curves that after tempering at any temperature, up to, say, 450° C., there always remains in solution an appreciable amount of carbon, which is reduced by raising the tempering temperature. After

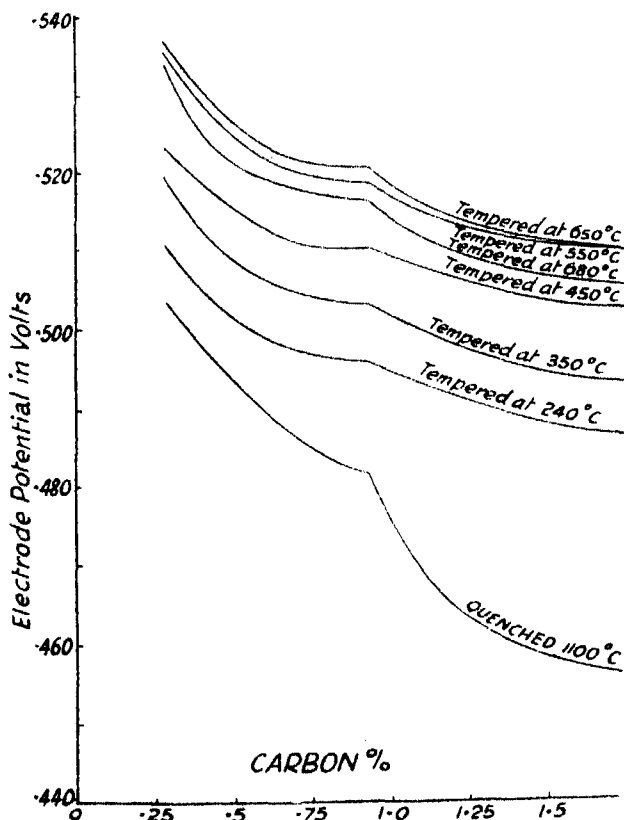


FIG. 3.—Electrode Potential of Quenched and Tempered Carbon Steels.

tempering for 3 hours at 240° C., the two series of steels were treated for a further 3 hours at the same temperature. This treatment did not, in general, decrease the amount of carbon in solution. The curves indicate that on heating quenched steels to a given temperature, tempering proceeds till a limiting value is reached, after which it ceases or proceeds extremely slowly. The same effect was observed by measuring continuously the change of resistance during the tempering of carbon and alloy steels.

From fig. 3, it will be seen that the electrode-potential curve obtained after tempering at 680° C. lies below the 650° C. curve, indicating that carbon dissolves in alpha iron below  $A_{c1}$ .

#### *Electrical Resistance.*

The determination of the specific resistance at ordinary temperature, of steels in various heat-treated conditions, was carried out as a preliminary to the investigation of the continuous change of resistance during tempering.

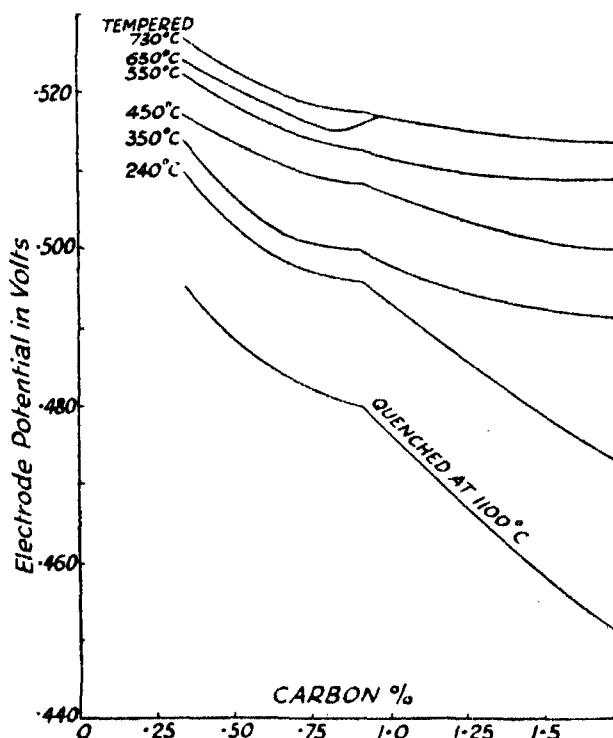


FIG. 4.—Electrode Potential of Quenched and Tempered Chrome Steels.

*Method of Measurement Employed.*—The determinations were carried out by passing a known current through a long, narrow cylindrical specimen and measuring the voltage drop between two knife-edges, which were a known distance apart and in contact with the specimen. The specific resistance, at the temperature of the test, was obtained by calculation from the diameter of the specimen and the distance between the knife-edges.

Since the specific resistance is inversely proportional to the square of the radius, it is necessary that the radius should be accurately known; and if the

specimen is only a few millimetres in diameter it is difficult to measure it with great accuracy. In spite of this fact, the specimens used in this investigation were thin, for in practice it is essential that the specimens be comparatively short and thin, as otherwise they bend or crack on quenching.

*Experimental.*—The specimens, which were 9 cm. long and 3 mm. in diameter, were of the same composition as those used in the electrode potential determinations.

The first step in the investigation was the measurement of the resistance at

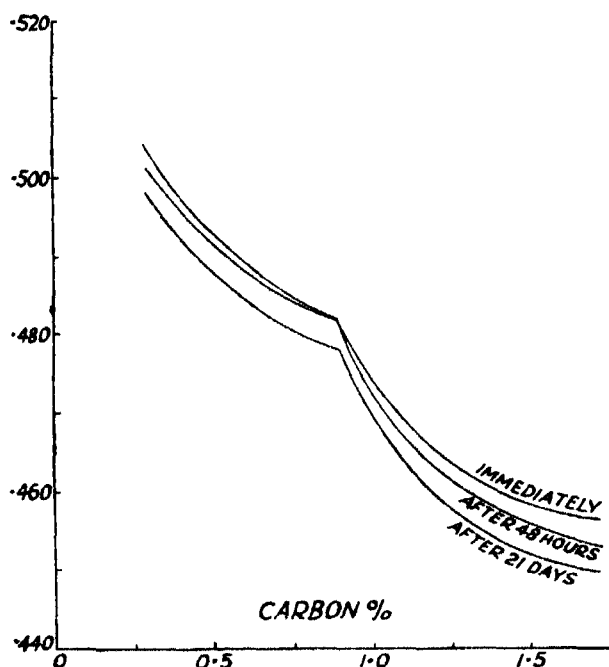


FIG. 4A.— Variation with Time of Electrode Potential of Carbon Steels, quenched at 1100° C.

17° C. of an annealed specimen, which was to be used as a standard during the experiments. For this purpose, the specimen was held down firmly by powerful elastic bands on two knife-edges, which were rigidly fastened 5 cm. apart on a wooden block. A Beckmann thermometer was placed in contact with the specimen, which was enclosed in a box so that its temperature could be accurately measured. A shunt of 0.1 ohm resistance was put in series with the standard, and a current of 1.5 amperes, taken from a battery of accumulators, was allowed to flow through the circuit. The potential drop between the knife edges was measured with a potentiometer, and the value of the

current was obtained with a second potentiometer, by reading the fall of potential between the terminals of the shunt. The resistance of the specimen at the temperature of the experiment was obtained by calculation.

Readings of resistance were taken during several days, the temperature at each experiment being read to one-hundredth of a degree. The results of the standardisation were plotted, and the resistance of the standard specimen at 17° C. was obtained from the curve.

*Measurement of the Resistance of the Heat-Treated Specimens.*—The heat-treated specimen, the resistance of which was required, was held firmly on a second pair of knife-edges, similar to that described above, by means of elastic bands, and was joined in series with the standard. The current, which had been flowing through an alternative circuit till fairly constant, was switched through the specimens, and the potential drop across 5 cm. of the standard was read on the potentiometer before and after that across 5 cm. of the unknown, simultaneous readings of the current being made in each case.

On the completion of this group of readings, the current was diverted through the alternative circuit, and the specimen was moved several millimetres on the knife-edges. A second series of readings was then taken as before.

Several groups of readings were taken for each specimen, the number depending on the uniformity of the steel. From each group of readings, the resistance of the specimen at 17° C. was calculated, and the mean of these values was taken as the resistance of the specimen.

The mean cross-sectional area of the specimen was obtained by measuring the diameter at 36 equal intervals along and around the specimen with a micrometer screw gauge. The quarter square of each reading was found, and the mean of the quarter squares was taken as the square of the radius of the specimen.

#### *Specific Resistance. Consideration of Results.*

From fig. 5 it will be seen that in *hypereutectoid* steels, the specific resistance is increased by raising the quenching temperature. This is in accordance with the iron-carbon diagram.

Campbell (6) and Saldau (7) found that in *hypoeutectoid* carbon steels, raising the quenching temperature increased the specific resistance. On the other hand, Le Chatelier (8), Benedicks (9) and McCance (10) found that this treatment caused no increase in specific resistance. The results of the present authors indicate that raising the quenching temperature decreases the specific resistance of these steels.

A straight line can be drawn through the values for the carbon steels quenched at 1100° C., in spite of the fact that the nature of the constituents varies from end to end of the series. It is evident that the resistance of steel is only affected by the amount of carbon in solution, and not by the nature and relative amounts of the constituents, martensite and austenite.

The values for the annealed carbon steels lie on a curve that shows a break at the eutectoid concentration. Beyond this percentage of carbon, the resistance increases less rapidly with the carbon content. It is apparent that the

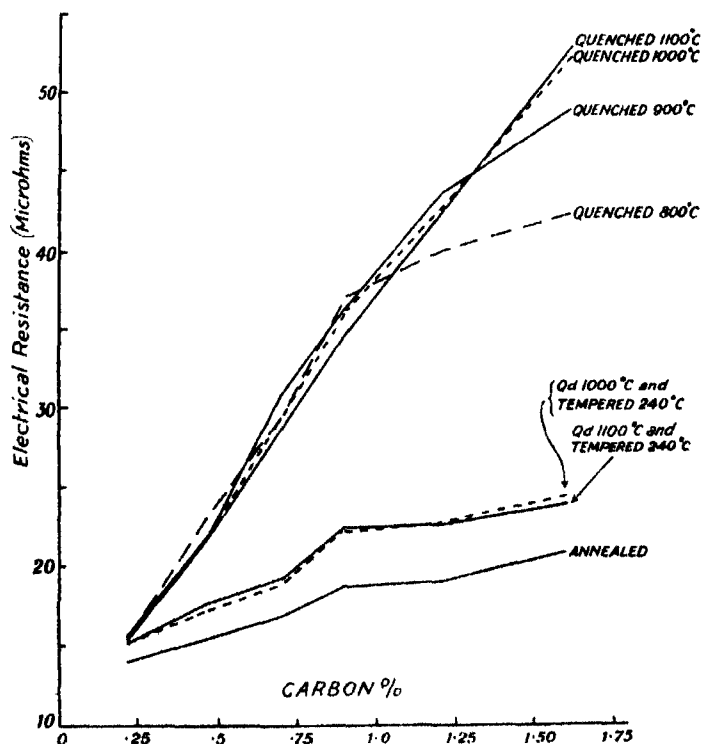


FIG. 5.—Electrical Resistance of Carbon Steels.

amount of carbon dissolved in alpha iron increases with the carbon content up to 0.9 per cent., but that further additions produce only free cementite.

The specific resistance of carbon steels tempered for 6 hours at 240° C. is also shown in fig. 5. It is clear that some carbon still remained in solution in the tempered steels, though tempering was practically complete for that particular temperature.

The specific resistances have been plotted without making corrections for sulphur, silicon, or phosphorus. The percentages of these elements present



in the steels were approximately constant in each series. In order to compare the results with those of other workers, however, the following corrections must be applied :—

1 per cent. of silicon raises the resistance 13·5 microhms (Burgess, Gumlich, and Le Chatelier).

1 per cent. of phosphorus raises the resistance of iron 11·0 microhms (D'Amico).

1 per cent. of manganese raises the resistance 5·5 microhms (Barrett, Lang, and Matsushita).

The values for the specific resistance of the carbon steels quenched at 1100° C., corrected according to these figures, lie on a line that can be expressed by the equation :—

$$R = 7.5 + 26.7 \times \text{carbon content.}$$

This agrees excellently with Benedicks' formula. The present authors, however, did not find that Benedicks' equation could be applied to special steels.

In the equation for quenched carbon steels, the specific resistance of iron is assumed to be 7·5 microhms. This value is obtained by extrapolation of the resistance curve of the quenched steels. Thompson (11) found 7·3 to be the specific resistance of pure iron. On the other hand, the extrapolated curve for annealed steels, as determined in the present experiments, meets the resistance axis between 9·5 and 9·9 microhms. Guillet (12), Gumlich (13) and Yensen (14) found the resistance of pure iron to be between these values.

Fig. 7 shows the specific resistance of the carbon and special steels quenched at 1000° C. The curves for the nickel and chromium steels practically coincide. When the relative positions of these curves in the annealed state (fig. 6) are compared, it is evident that chromium is completely in solution only in the quenched state, whereas nickel remains in solution both in the annealed and in the quenched states.

An examination of the curves for quenched and annealed steels shows that in every case the curve for nickel-chromium steels lies above the others. It can be shown that in a nickel chromium steel of given carbon content, the resistance is increased above that of a corresponding carbon steel, by an amount equal to the sum of the increases due to each of the special elements. Thus, in the steels containing 0·51 per cent. of carbon, taking the actual resistance of the carbon, chromium and nickel steels from the curves, and allowing for the difference in the percentage of nickel and chromium in the

nickel-chromium steel, the calculated resistance of the latter is 37·5 microhms. The value actually found for this steel was 37·6 microhms. Similarly, the calculated resistance of a nickel-chromium steel containing 1 per cent. of

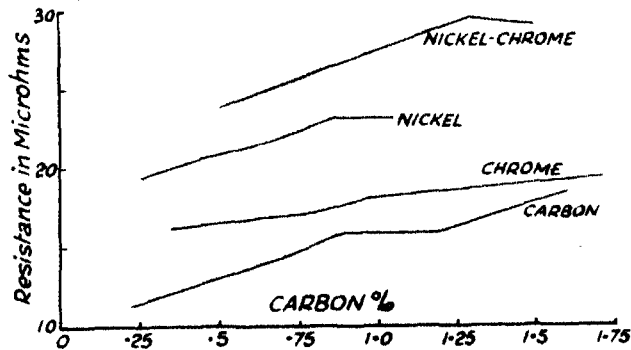


FIG. 6.—Electrical Resistance of Annealed Steels.

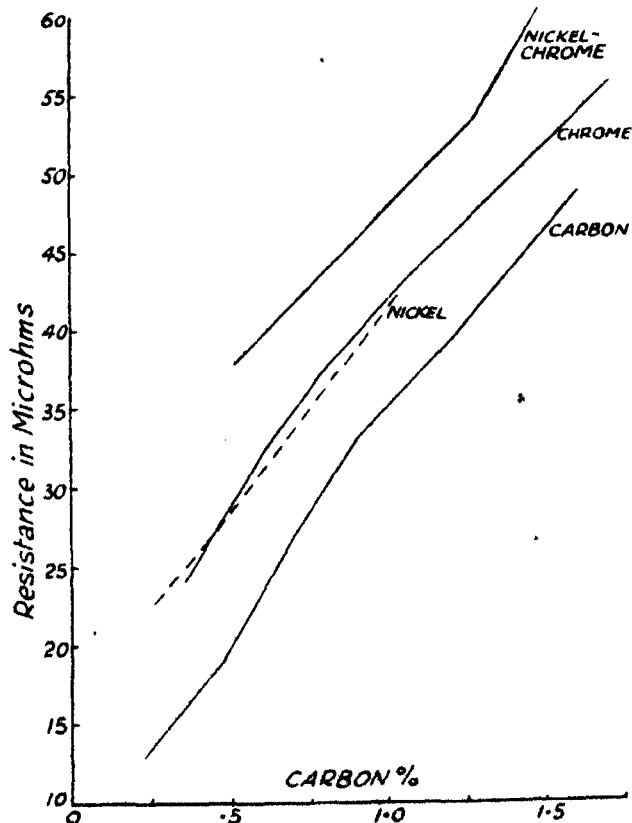


FIG. 7.—Electrical Resistance of Steels, quenched at 1000° C.

carbon is 49.0 microhms, as compared with the experimentally-found value of 48.0 microhms.

In the course of the present work it was found that the effect of special elements on the resistance of steel depended on whether the steel was quenched or annealed, and on the quenching temperature and carbon content. Thus, the addition of 1 per cent. of chromium increased the resistance of quenched steels by about 4.6 microhms, when the carbon content was less than 1 per cent. Above this percentage of carbon the effect of chromium became gradually less, until at 1.6 per cent. carbon, the increase in specific resistance was only 3.3 microhms. In the annealed steels the effect of chromium was considerably less than either of these values, and varied noticeably with the carbon content. This is not in agreement with Benedicks' formula.

In low-carbon nickel steels (fig. 8) 1 per cent. of nickel increased the specific resistance by 2.3 microhms. In high-carbon steels the corresponding increase was about 1.9 microhms. This applied equally to the quenched and annealed steels. According to Benedicks' formula 1 per cent. of nickel should increase the resistance by 5.4 microhms.

From figs. 8, 9 and 10 it will be seen that in the case of special steels, increasing the quenching temperature increases the specific resistance of hypereutectoid steels and decreases that of hypoeutectoid steels.

The results obtained for the chromium steel containing 1.73 per cent. of carbon, quenched from 1000° C. and 1100° C. respectively, are peculiar; for the higher quenching temperature gave the lower resistance. Similarly, a nickel steel containing 1 per cent. of carbon gave a higher specific resistance when quenched from 900° C. than when quenched from higher temperatures, indicating that martensite has a higher specific resistance than austenite. In order to throw light on this point a number of high-carbon special steels were quenched from 1100° C. and immersed in liquid air for one hour. The specific resistance of each specimen was measured before and after immersion, and the following results were obtained:—

Chromium steel B (1.73 per cent. carbon) : Resistance fell 0.4 microhm.

Nickel-chromium G1 (1.28 per cent. carbon) : Resistance fell 1.1 microhms.

Nickel-chromium G2 (1.51 per cent. carbon) : Resistance fell 3.0 microhms.

This indicates that martensite has a lower specific resistance than austenite, for specific volume measurements (15) showed that the austenite in the quenched steels had been largely converted to martensite by immersion in the liquid air. On the other hand, during the determination of the tempering-resistance curves, evidence was obtained that at 240° C. martensite has a

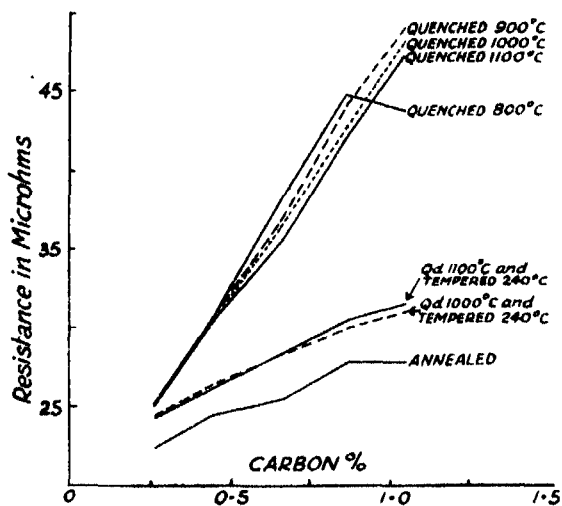


FIG. 8.—Electrical Resistance of Nickel Steels.

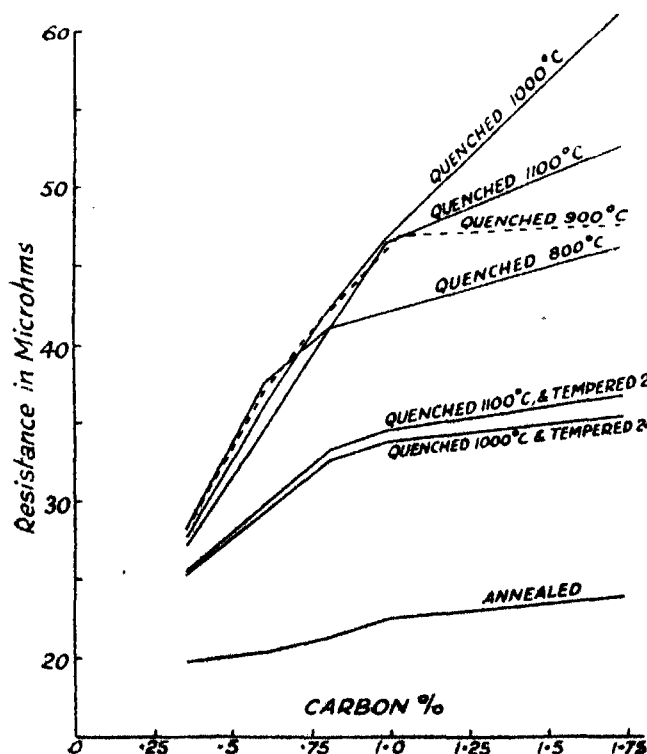


FIG. 9.—Electrical Resistance of Chrome Steels.

higher specific resistance than austenite. These results indicate a difference in the nature of martensite according to its temperature of formation.

*Measurement of Resistance during Tempering.*

In order to investigate the reactions that occur during the tempering of steel the process was watched by measuring the resistance of steel specimens at the closest possible intervals of time, during several hours. Before the method finally adopted was devised, a number of preliminary experiments

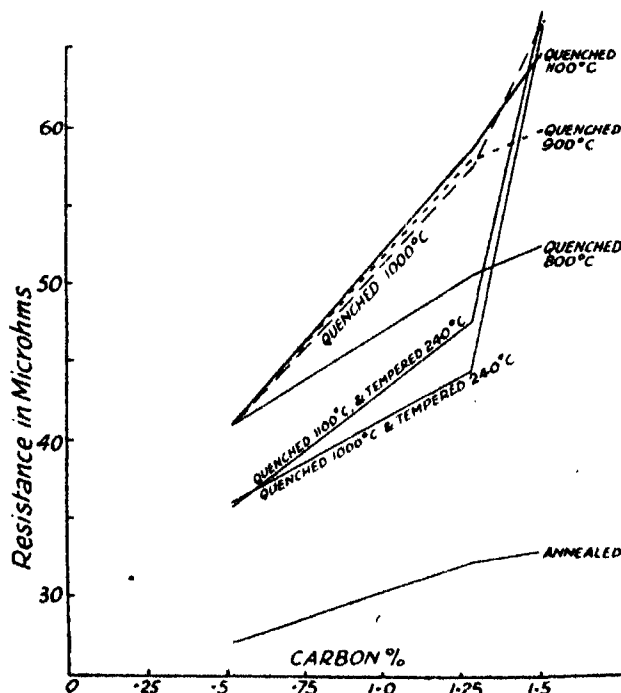


FIG. 10.—Electrical Resistance of Nickel-Chrome Steels.

were performed, and it became evident that several factors required careful attention. In the first place the temperature had to be kept constant at the working heat, otherwise small changes of resistance would have been obscured. Secondly, the tempering of martensite proceeds with great rapidity, and the greatest change takes place in the first few minutes, so that it was essential that readings should be taken immediately tempering commenced.

The general layout of the apparatus is shown in fig. 11. For descriptive purposes the apparatus may be dealt with most conveniently in three sections.

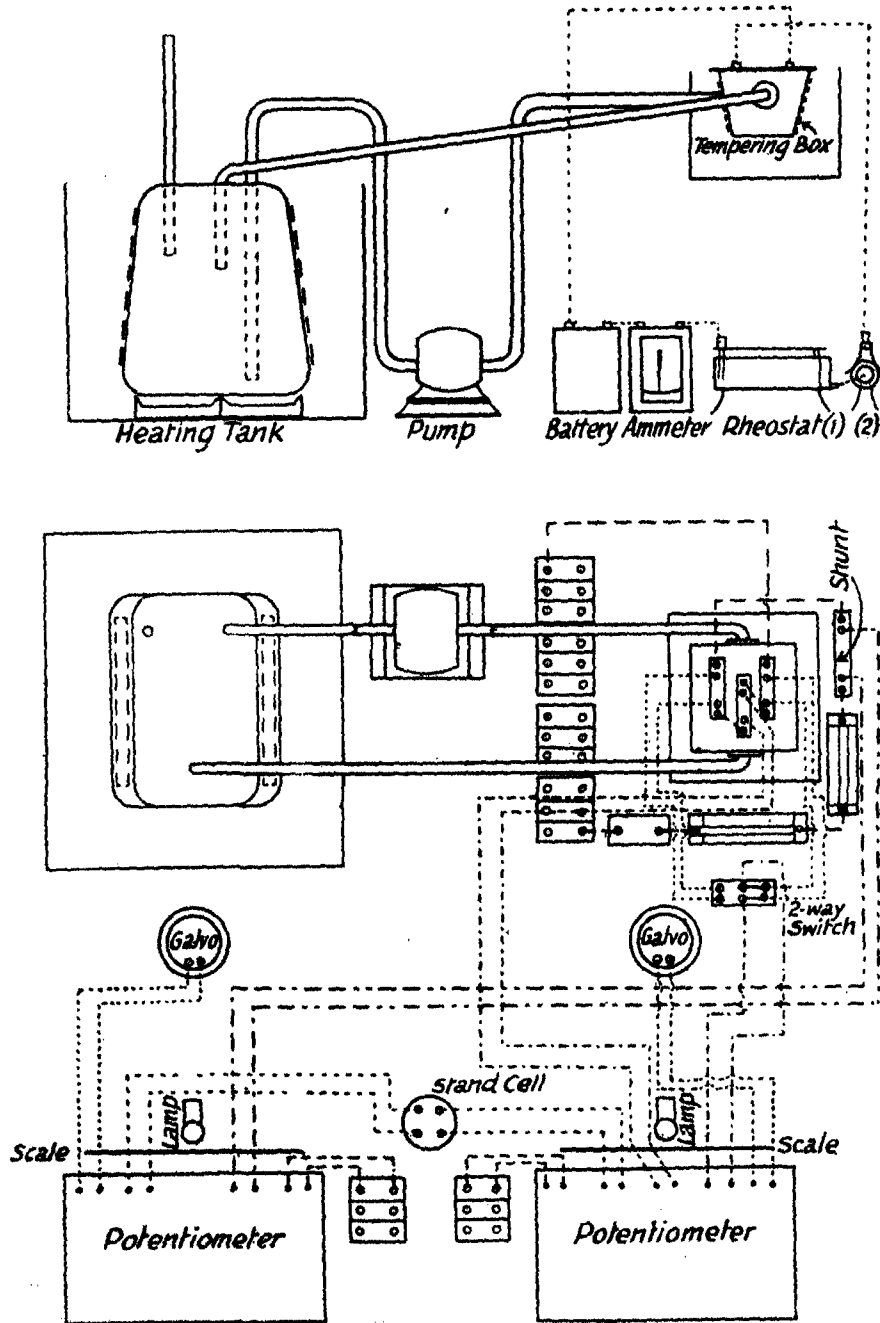


FIG. 11.—Tempering-Apparatus.

*The Oil Heating and Circulating System.*—A copper tank containing about 4 gallons of heavy cylinder-oil was heated electrically by means of nichrome elements and resistance mats. The oil was pumped from the heating tank by means of a sud pump into one end of a brass box of small capacity, in which the specimens were suspended. A baffle plate provided equal distribution of the hot incoming oil. From the other end of the tempering box the oil flowed under gravity back into the heating tank.

Two cast-brass lids were provided for the tempering box. One of these carried the terminals, knife-edges and current connections, in addition to a thermometer. The second lid was provided with a hole for a thermometer only. Prior to an experiment the second lid was kept in position till the temperature was steady. To minimise heat losses both tanks were packed in asbestos wool, and the system of pipes was heavily lagged. The temperature of the oil in the tempering box was adjusted by regulating the current flowing through the heating elements.

*The Current Supply System.*—The resistance of the specimen was measured by finding the voltage drop across a length of 5 cm. Although it was not found possible to get a source of current which was perfectly invariable, a battery of twelve 1.3 volt "Nife" cells proved very consistent. The current circuit included an ammeter (for rough measurement), two rheostats (for adjusting the current to the desired value, 1.5 amperes), a standard shunt of 0.1 ohm resistance, the standard specimen and one unknown. Accurate measurement of the current was obtained by reading on a potentiometer the drop in volts across the shunt.

*Electrical Measuring Apparatus.*—Two Tinsley Vernier potentiometers were used to measure the drop in volts across the standard specimen, the unknown specimens, and the shunt. Details of the connections are shown in fig. 11.

As a result of the method used for fixing the specimens to the lid of the tempering box, it was not possible to set the knife edges a definite distance apart—a distance piece did not give sufficient accuracy. This difficulty was overcome by measuring the specific resistance of the specimen at 17° C. by the method described under "Electrical Resistance," and then attaching the specimen to the lid with the knife edges approximately 5 cm. apart, and measuring its resistance at 17° C. From the data thus obtained, the exact length of the specimen was calculated.

*Determination of the Resistance of the Standard Specimen.*—The first step in carrying out the investigation was to determine the resistance of an annealed specimen at the tempering temperature, which was fixed at the convenient

value of 240° C.—this being the temperature at which the apparatus attained its greatest constancy.

The specimen was fixed between the knife edges on the lid. Each end was wrapped in lead foil and tightly gripped by the clamps to which the current connections were attached. The lid was then placed in position on the tempering box, through which the heated oil was flowing, and the resistance of the standard was obtained by taking a large number of simultaneous readings of the current and of the voltage drop between the knife edges. The temperature of the oil, which was read by means of a mercury thermometer, was varied from several degrees below 240° C. to several degrees above, and the resistance of the standard at 240° C. was found by plotting all the values obtained against the corresponding temperatures, and reading off the value at 240° C.

*Procedure during the Experiments.*—Although the whole of the apparatus was thoroughly lagged, it required about five hours to heat up to 240° C. and to become steady at that temperature. In order that work could be started at 9.30 a.m., and that a whole day should be available for the tempering, it was necessary that heating should begin at 4.30 a.m. Moreover, the cylinder oil was so viscous at low temperatures that the circulating system could not be started in the cold. The following arrangements were therefore made for starting :—

An alarm clock, set to ring at 4.30 a.m. released a “ Little Nipper ” rat trap, which pulled the main switch for the heating coils. At the same time, it pulled the catch on a second clock into the alarm position. This alarm was set for 6.30 a.m., and at that time it started the oil-pump motor. By 9.30 a.m. all preparations for the experiment had been made, and the current, which had been running for about half an hour, had reached satisfactory constancy after the usual initial period of fluctuation. No further readings of the current were taken, since this factor was eliminated by taking simultaneous readings of the voltage drop across the standard and the quenched specimen by means of the two potentiometers.

The lid was now placed in position on the box, so that the specimens were immersed in the oil, and readings of the voltage drop across each of the specimens were taken one-half minute after immersion, at intervals of a half minute thereafter up to ten minutes, at intervals of one minute till twenty minutes, and as frequently thereafter as seemed desirable.

The specific resistance of the tempering specimen at 240° C. was calculated, at each reading, by means of the formula—

$$R'_t = \frac{E'_t \times R \times a}{E_t \times l}$$



where  $R'_t$  == specific resistance of the tempering specimen at time  $t$ ,  
 $R'_t$  == volt drop across 5 cm. of tempering specimen at time  $t$ ,  
 $E_t$  == volt drop across 5 cm. of standard specimen at time  $t$ ,  
 $R$  == resistance of the standard at 240° C.,  
 $a$  == cross-sectional area of the specimen,  
 and  $l$  == length of the specimen.

As will be seen from the formula, the true specific resistance of the specimen at 240° C. is obtained, if it is assumed that the temperature coefficient of the standard is the same as that of the hardened specimen. This assumption is, of course, not correct; but, as the temperature of the oil bath did not, at any time after immersion, differ from 240° C. by more than  $\pm 2^\circ$  C., the error introduced is negligible.

The specific resistance of each tempered specimen at 17° C. was measured between the standard knife-edges, after withdrawal from the oil.

*Determination of Resistance at Zero Time.*—From consideration of the results obtained during the measurement of the change of resistance at 240° C., it became evident that the fall of resistance during the first few minutes was often very great, and extrapolation of the tempering curve to meet the resistance axis, in order to obtain the starting point of the reaction, would not be justifiable. The specimens were therefore re-quenched, and their temperature coefficients measured between 0° C. and 80° C. For this purpose, the specimens were immersed in a water bath, the temperature of which was gradually raised by the addition of boiling water. Readings of resistance were taken every few degrees, the temperature being allowed to become steady before each measurement. The values were plotted, and the temperature coefficient of resistance was calculated from the line through the points. The specific resistance of the quenched specimen at 240° C. was then calculated, and this was taken as the starting point of the reaction.

#### *Consideration of Results.*

By the method described above, the tempering-resistance curves of the carbon, nickel, chromium, and nickel-chromium steels, quenched from 900° C., 1600° C., and 1100° C., were determined. In all, 46 specimens were examined, but as the curves are all of a similar type, those shown in figs. 12 and 13 will be sufficient to demonstrate the general form.

In fig. 12 a series of curves representing the tempering of carbon steels is shown. The curve for the steel containing 1.61 per cent. of carbon is representative of steels in which some austenite has been retained by quenching; the

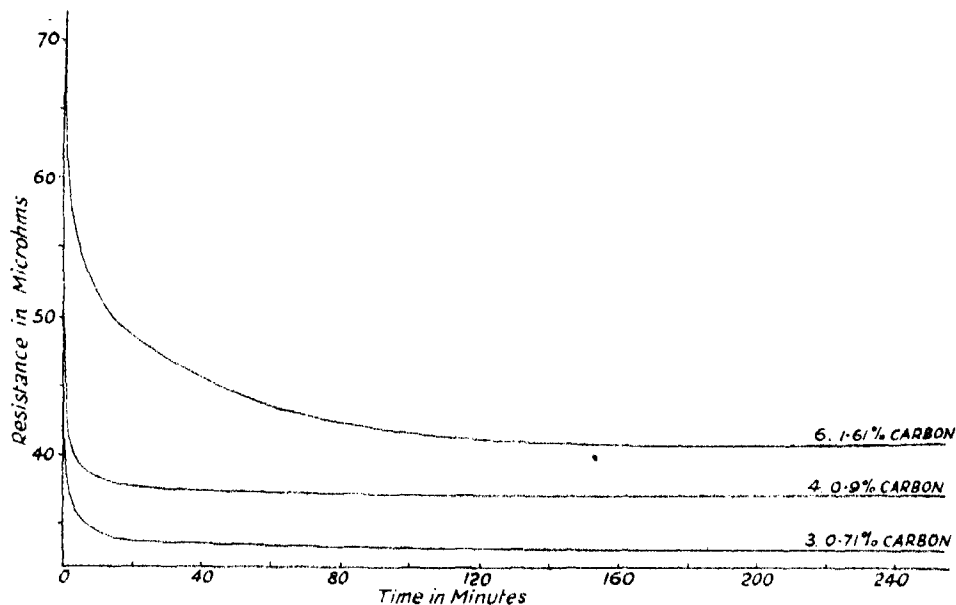


FIG. 12.—Change of Resistance during Tempering of Carbon Steels, quenched at 1000° C.

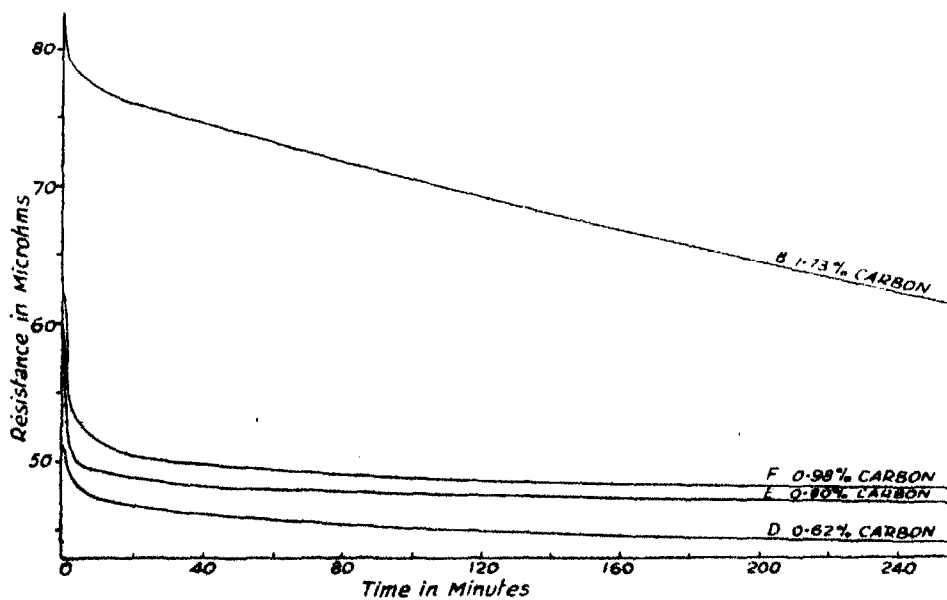


FIG. 13.—Change of Resistance during Tempering of Chrome Steels, quenched at 1000° C.

other curves in this figure are typical of the tempering of martensite. In fig. 13, in which a series of curves for chromium steels is shown, that of the steel containing 1.73 per cent. of carbon is typical of the curves of steels that are mainly austenitic; whereas the others are similar to the curves of the martensitic carbon steels.

The tempering of steel appears to consist of a number of concurrent reactions, and though each of these is in itself simple, the cumulative effect, as measured by the change of electrical resistance, is not immediately reducible to simple terms. On account of the mutual dependence of the reactions, it is not possible experimentally to measure the progress of each separately, and recourse must be had to some method of resolving the resultant curve into its components. A method of analyzing the tempering-curves will now be described.

The martensitic and austenitic steels give rise to markedly different curves, and must be considered separately. Exact knowledge of the behaviour of martensite is necessary before the analysis of the curves for steels containing both martensite and austenite can be attempted. It is, therefore, convenient to consider first the curves of the purely martensitic steels.

The process of tempering in martensitic steels may be divided into three reactions. The first of these is the separation of carbon from solution, accompanied by a fall in resistance proportional to the amount separating. The precipitated carbon is not removed from the system, but remains present as free carbide, the accumulation of which results in an increase of resistance proportional to the amount of carbon precipitated. This constitutes the second reaction. These two reactions proceed simultaneously, and give rise to an initial rapid fall of resistance. The state attained at the end of the primary rapid separation of carbon is not permanent, but the subsequent reaction is slower, and can be conveniently isolated. This final reaction is accompanied by a gradual fall of resistance, probably due to a gradual increase in the size of the precipitated particles. These three simple processes combine to give the experimentally determined curves.

In resolving the tempering-curve into its components, the first step is to determine the point at which the first rapid change is completed. As the two changes overlap and lose their identity imperceptibly, the selection of this point is purely arbitrary. Thus, any point between 20 and 30 minutes could be selected with equal justification. For the present purpose the junction between the different reactions has been assumed to occur at 26 minutes.

By means of the known values of the resistance of the carbon steels as quenched, and after tempering for 26 minutes, the first portion of the curve

was divided into its components. The values for the specific resistance at  $240^{\circ}\text{C}$ . of the quenched carbon steels—that is, the resistance at zero time on the tempering-curves—were plotted, and the best straight line through the points was drawn. (AO, fig. 14.) Similarly, the best straight line through the values for the same steels after tempering for 26 minutes at  $240^{\circ}\text{C}$ . was

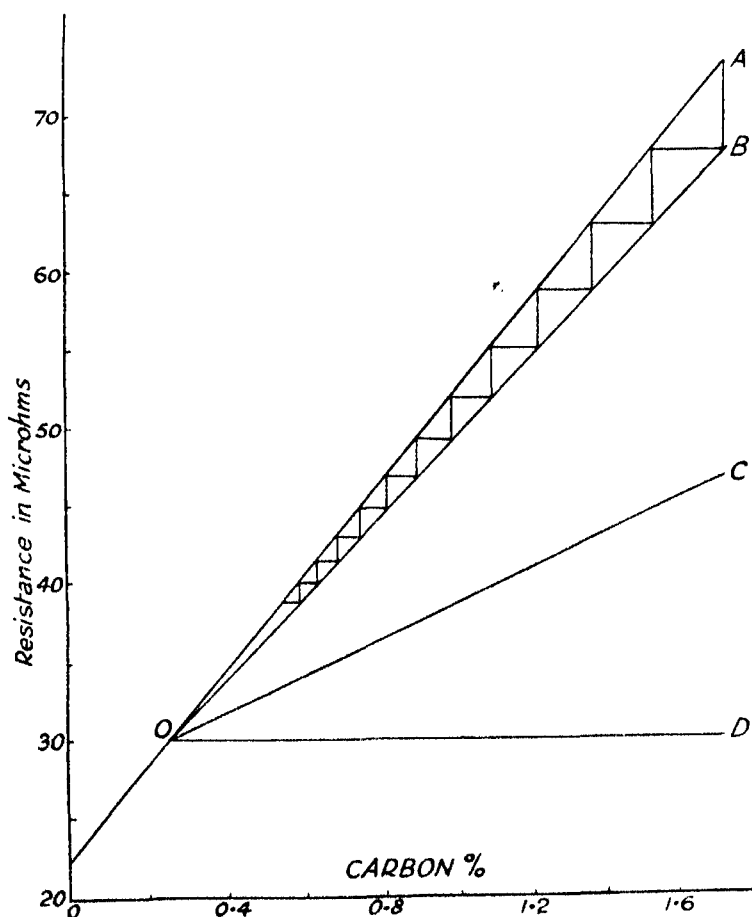


FIG. 14.

drawn. (CO, fig. 14.) These lines meet at a point O whose co-ordinates are 30 microhms and 0.24 per cent. of carbon, indicating that, on tempering for 26 minutes at  $240^{\circ}\text{C}$ ., there is no change in the resistance of a steel containing 0.24 per cent. of carbon, or that a carbon steel, after this period of tempering, retains 0.24 per cent. of carbon in solution. From this it may be deduced that the specific resistance of a quenched steel containing 1.73 per cent. of carbon

would fall from 73 microhms (point A) to 30 microhms (point D) in 26 minutes, if the carbon, on separating, were removed from the system. The carbon, however, is not removed, and its effect in raising the resistance is represented by the line through the values for steel tempered 26 minutes at  $240^{\circ}\text{C}$ . Thus, the specific resistance of the tempered steel containing 1.73 per cent. of carbon would be raised from 30 microhms to 47 microhms (point C) by the presence of the accumulated cementite. The total effect of the tempering is, therefore, a drop of 26 microhms (A to C) made up of a fall of 43 microhms (A to D), and a rise of 17 microhms (D to C) (fig. 14).

To resolve the experimentally determined curves into the two components it is necessary to multiply the observed drops by  $43/26$  to obtain the fall of resistance due to separation of carbon, and by  $17/26$  to obtain the rise of resistance due to the free carbide formed.

If the rate at which carbon comes out of solution is proportional to the amount of carbon in solution, the component curves representing the fall of resistance due to separation of carbon from any martensitic carbon steel should form part of one general curve. On resolving the time-resistance curves for the martensitic carbon steels into two components in the manner described, it was found that these components did conform to a general curve; but this curve, when obtained by the method just described, did not extend beyond 1.19 per cent. of carbon, for the steels containing more than that percentage were not entirely martensitic, and the method was only applicable to martensitic steels. Before proceeding to the next step it was necessary that the general curve should be extended from 1.19 to 1.73 per cent. of carbon.

If the rate of separation of carbon from martensite is proportional to the amount of carbon in solution, the resistance of the steels in the carbon series will be represented at any time between zero time and 26 minutes by a straight line through the pivot point O. It can therefore be assumed that if the quenched carbon steels were tempered for a given interval of time, the resistance of the specimens would be represented by a line such as BO (fig. 14). Making this assumption, the general curve for the fall of resistance, due to separation of carbon from martensite, can be determined by a simple geometrical method. Thus, by stepping down the line as shown in fig. 14, the drops of resistance in successive equal intervals of time may be found. The vertical lines between AO and BO represent the successive drops in specific resistance in successive, equal time intervals. The horizontal lines between AO and BO represent the successive drops in the amount of carbon in solution. The theoretical general curve was obtained in this manner, by plotting the fall of resistance, or the

fall of concentration of carbon in solution, against time. This curve extended to 1.73 per cent. of carbon ; but the units of the time axis were unknown, since the time interval between AO and BO was not known. However, a general curve extending to 1.19 per cent. of dissolved carbon had been derived from the experimental tempering curves, as described earlier ; and by adjusting the time axis of the new curve, the two curves were made to coincide accurately for the interval representing the tempering of a 1.19 per cent. carbon steel, thus determining the time axis of the theoretical curve. The theoretical general curve, showing the rate at which the resistance of martensite falls at 240° C. due to separation of carbon, is shown in fig. 15. This curve applies to martensite containing up to 1.73 per cent. of carbon.

In a similar manner, the general curve representing the rise of resistance due to accumulation of the separated carbide was obtained, and is shown in fig. 16.

From fig. 14, the rate at which carbon comes out of solution was determined by multiplying the drops in resistance per minute by a factor expressing the ratio between carbon in solution and resistance. This factor was obtained from the slope of the line AO in fig. 14, and was found to be 0.03334. The curve obtained in this manner, representing the rate at which carbon is precipitated from martensite at 240° C., is shown in fig. 17. By the same method, the corresponding curves for the nickel, chromium, and nickel-chromium steels were obtained. These curves are shown in figs. 15, 16 and 17.

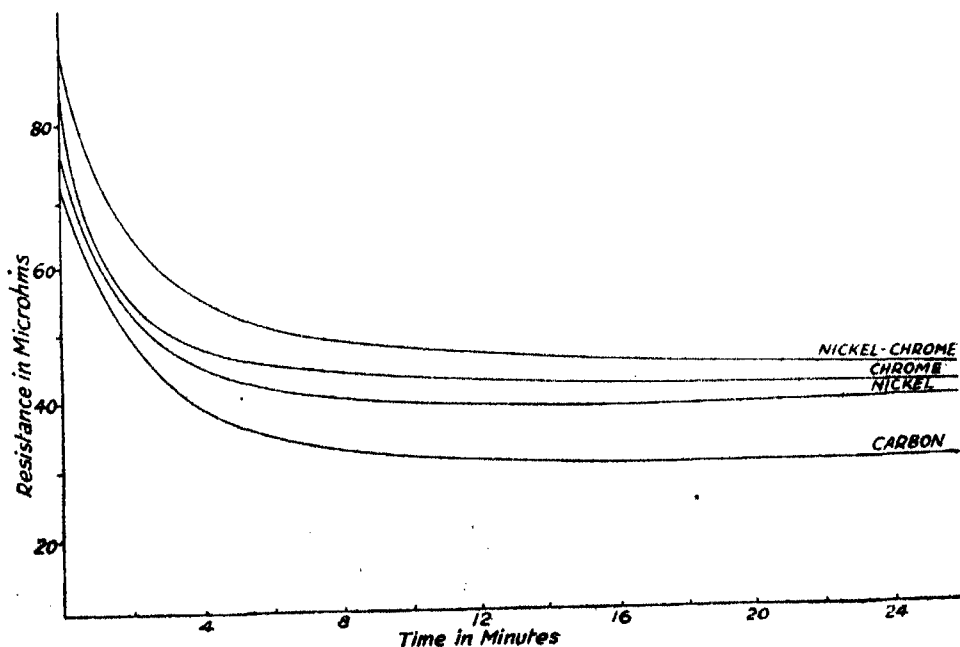


FIG. 15.—Rate of Fall of Resistance in Martensitic Steels.

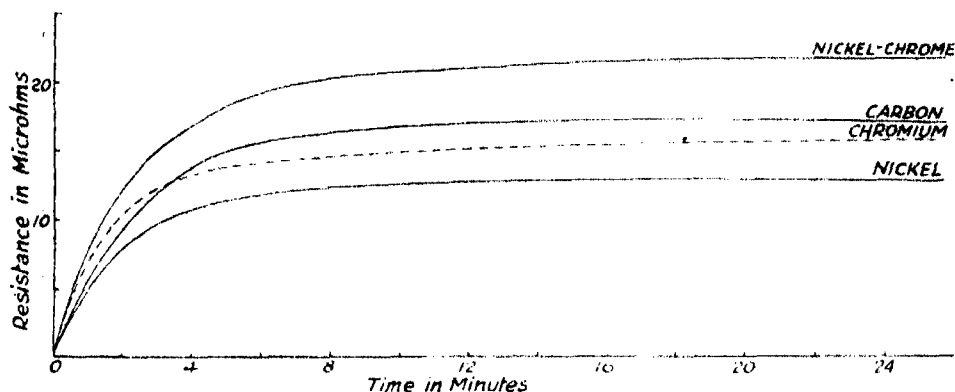


FIG. 16.—Rate of Rise of Resistance due to Accumulation of Precipitated Carbide in Martensitic Steels.

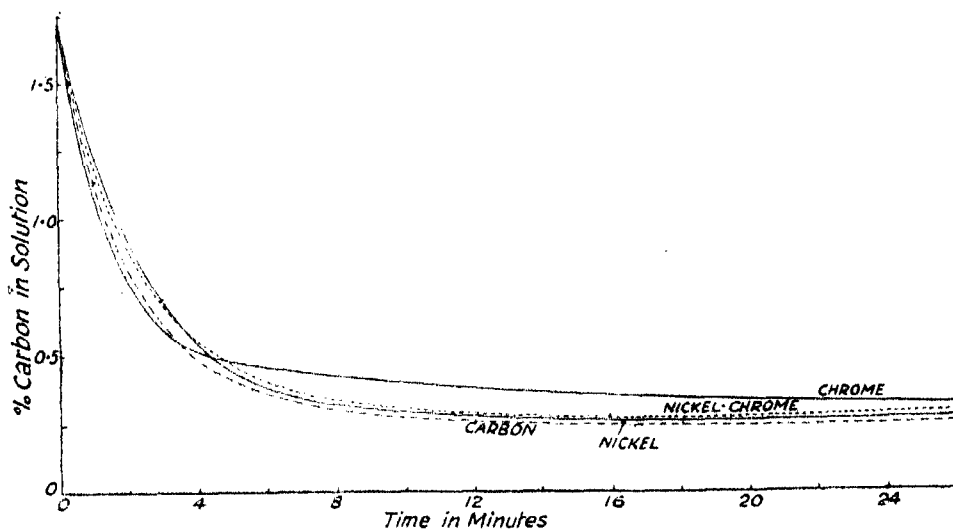


FIG. 17.—Rate of Separation of Carbon from Martensitic Steels.

By means of the curves plotted in figs. 15, 16 and 17 it is possible to construct the tempering-resistance curve of any steel within the limits of composition of the steels examined. As a check on the work, the curves derived in this way were compared with the tempering curves that had been determined experimentally. Except for a few points at the beginning of each curve, the agreement was satisfactory. The lack of agreement at the beginning of the reaction is probably due to the method of deriving the theoretical curve. The line AO in fig. 14 represents the best line through the first values on the tempering curves.

These values were calculated from the known resistance of the quenched steels at 15° C. and their temperature coefficient of resistance. It is possible that the slight error introduced by this method of determining AO may be responsible for the discrepancy at the beginning of the curves.

The experimental curve for the carbon steel containing 1·61 per cent. of carbon (fig. 18, Curve A) does not agree with the theoretical tempering curve

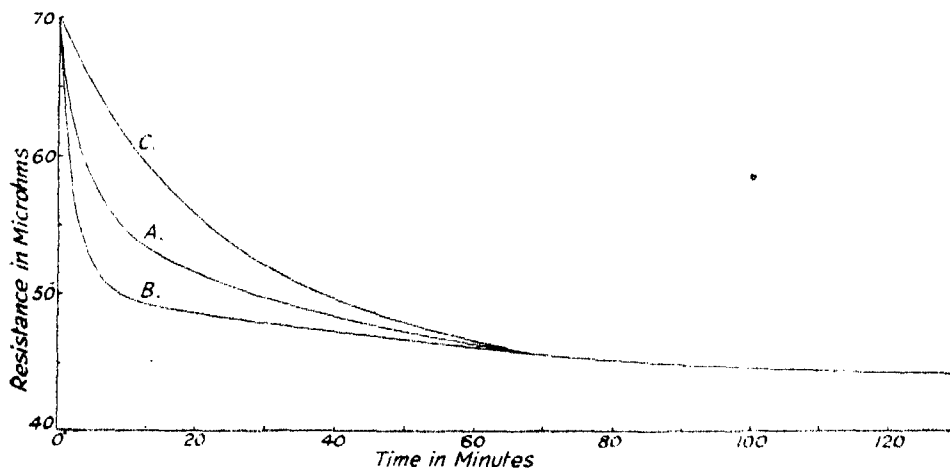


FIG. 18.—Rate of Fall of Resistance in Steel containing 1·61 per cent. Carbon: (A) as quenched: (B) if wholly martensitic: (C) if wholly austenitic.

as derived by the method described above (fig. 18, curve B). This steel is only distinguished from the other carbon steels by the presence in it of a considerable amount of austenite. As this steel when quenched was not entirely austenitic, the experimental curve does not represent the tempering of pure austenite, but of a mixture of austenite and martensite in unknown proportions. This curve is, therefore, the resultant of two curves, which represent respectively the tempering of martensite containing 1·61 per cent. of carbon, and of austenite of similar composition. One of these components may be obtained from the theoretical tempering curve of martensite in a 1·61 per cent. carbon steel (fig. 18) by the following method :—

The theoretical tempering curve shows that if the steel consisted entirely of martensite, the specific resistance would fall from 70 microhms to 49·4 microhms in the first 12 minutes of tempering. From the experimental curve it is seen that the resistance actually fell from 70 microhms to 53·5 microhms. The greater part of this fall was due to the tempering of martensite, which tempers rapidly, but a part was also due to the slower tempering of austenite. The fall



of resistance due to tempering of austenite during the first 12 minutes may be found by extrapolation. In the case of the austenitic carbon steel the extrapolation is difficult, because of the large change that occurs during that interval of time, but in the case of the special steels the extrapolation is much more accurate. However, if the experimental curve is extrapolated back from 12 minutes to zero time, it meets the resistance axis at 57.5 microhms. The change of resistance arising from the tempering of austenite in the first 12 minutes is therefore  $57.5 - 53.5$ —that is, 4 microhms. The change of resistance attributable to tempering of martensite is therefore 12.5 microhms. If the steel had been entirely martensitic, the change would have been 20.6 microhms. The change in resistance due to the tempering of martensite in the quenched steel is  $\frac{12.5}{20.6}$  of the change that would occur if the steel were totally martensitic.

By taking the drops of resistance in intervals of one minute on the martensitic curve (Curve B, fig. 18) and multiplying each drop by  $\frac{12.5}{20.6}$ , the martensitic component of the experimental curve was obtained; and by subtracting the drops per minute on this component curve from the actual drops on the experimental curve, the austenitic component was obtained. The relation which the austenitic component bears to the curve that would be obtained if the steel were entirely austenitic is similar to that which the martensitic component bears to the curve for pure martensite. Thus, to obtain the curve that would represent the fall of resistance if the steel were entirely austenitic, the drops per minute on the austenitic component may be multiplied by  $\frac{20.6}{8.1}$ .

Curve C (fig. 18) was obtained in this manner. The austenitic special steels were analyzed by the same method, and the curves showing the rate at which the resistance of austenite of the corresponding composition would fall at 240° C. were obtained.

The austenitic curves obtained as above were resolved into three components by the same method as was used for the martensitic curves.

As the fall of resistance is proportional to the amount of carbon coming out of solution, the rate at which the carbon separates may be calculated for each steel. Curves showing this rate for the various austenitic steels were calculated and are shown in fig. 19. When these curves were plotted on suitable time axes, they were found to coincide with the general curve for the separation of carbon from martensitic carbon steels. This indicates that the precipitation

of carbon from solution in gamma iron proceeds in the same manner as the precipitation of carbon from solution in alpha iron, though at a lesser rate. It was found by this method that the austenite in a carbon steel containing 1.61 per cent. of carbon, quenched at 1100° C., tempers 10 times more slowly than a martensitic carbon steel of the same carbon content; that in a nickel-steel containing 1.06 per cent. of carbon the austenite tempers 18 times more slowly than a martensitic carbon steel of the same carbon content; that the austenite in a chromium steel containing 1.73 per cent. of carbon tempers 66 times more slowly than a martensitic carbon steel of the same carbon

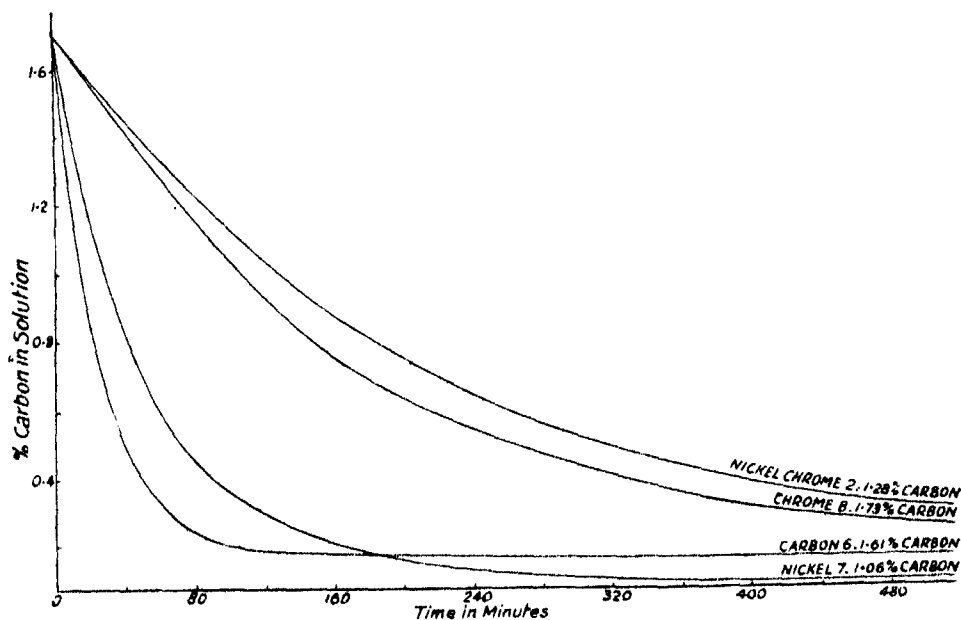


FIG. 19.—Rate of Separation of Carbon from Austenitic Steels.

content; and that in a nickel-chromium steel containing 1.28 per cent. of carbon it tempers 80 times more slowly than a martensitic carbon steel of the same carbon content.

It is clear that whereas martensite tempers very rapidly, austenite tempers slowly. It follows that during continuous tempering at any temperature, martensite cannot accumulate by the decomposition of austenite; in effect austenite tempers directly to troostite. It is commonly known that martensite is formed when an austenitic steel is heated at 240° C. and cooled. If the martensite so formed does not accumulate at the tempering temperature, it must form during cooling.

To decide this point, the following experiments were performed :—

While an austenitic chromium steel was tempering slowly, it was removed from the tempering-bath and allowed to cool to room temperature. When the specimen was replaced in the tempering-bath, the resistance was found to have risen, due to accumulation of martensite, which now tempered rapidly in the characteristic manner. The same experiment was performed with an austenitic nickel-chromium steel. These experiments indicate that the decomposition of austenite at constant temperature does not proceed in the same manner as during cooling. It might be contended that the relative tempering rates of austenite and martensite are reversed at some temperature below 240° C., but it has been conclusively shown by numerous investigators that at lower temperature austenite does not temper appreciably, whereas martensite tempers at any temperature above 100° C.

#### *Conclusions.*

In the work described in this paper there is much that substantiates commonly accepted beliefs ; and much that indicates that some of the fundamental conceptions which form the basis of our knowledge of steel are erroneous. Each point, as it arose, has been discussed in the text ; so, in order to avoid reiteration of commonplace facts, only those points that suggest the need for revision of generally accepted conceptions will be considered here.

The customary method of investigating the process of tempering consists of heating intermittently to the selected temperature, and making the required observations at room temperature between the periods of heating. The procedure is not strictly correct, for it involves periods of heating and cooling between each observation. It is commonly believed that the only effect of the heating and cooling is slightly to increase the effective time of tempering ; but the results obtained by the method of continuous measurement of resistance make it clear that, at any rate in the case of austenitic steels, the results given by the intermittent method of tempering do not show what happens at the tempering temperature.

From the tempering-resistance curves, it is evident that, as martensite tempers much more rapidly than austenite, martensite can never accumulate during tempering at the tempering temperature. The intermittent method would lead to the opposite conclusion ; for example, when an austenitic chromium-steel was tempered for 3 hours at 250° C., and cooled to room temperature, a considerable amount of martensite was found in the specimen. The martensite produced by this method must have been formed during cooling. The time

taken for the specimen to cool from 250° C. was considerably less than half-an-hour, and during this period, as can be seen from the tempering-resistance curve of the steel, the amount of tempering that would have occurred at 240° C. would have been very small; yet a considerable amount of austenite tempered to martensite during the cooling. The obvious deduction is that austenite can temper in two different ways: slowly at a constant temperature, and more rapidly when the temperature is falling. At a constant temperature, austenite appears in effect to temper directly to troostite; martensite is only retained when the austenite is decomposed by cooling. The rapid breakdown during cooling is of the same nature as the lower change point designated A'' by Portevin and others; the slow change at constant temperature is similar to that which occurs at the ordinary A<sub>1</sub> or A' point.

The determinations of the electrode potential of steels tempered at different temperatures, show that the state attained at the conclusion of tempering at

Table I.—Composition of Steels.

	C.	Mn.	P.	S.	Si.	Ni.	Cr.
CHROMIUM STEELS							
C.	0.35	0.24	—	—	0.17	—	1.58
D.	0.62	0.22	—	—	0.18	—	1.67
E.	0.80	0.28	—	—	0.20	—	1.67
F.	0.98	0.28	—	—	0.22	—	1.68
B.	1.73	0.30	—	—	0.21	—	1.65
CARBON STEELS.							
1	0.22	0.08	—	—	0.15	—	—
2	0.48	0.18	—	—	0.11	—	—
3	0.71	0.16	—	—	0.10	—	—
4	0.90	0.20	—	—	0.14	—	—
5	1.19	0.18	—	—	0.11	—	—
6	1.61	0.18	—	—	0.13	—	—
7	1.73	0.20	—	—	0.08	—	—
NICKEL STEELS.							
2	0.26	0.27	0.014	0.025	0.10	3.64	—
4	0.44	0.33	0.015	0.038	0.12	3.65	—
5	0.67	0.40	0.012	0.027	0.11	3.64	—
6	0.87	0.41	0.013	0.025	0.15	3.64	—
7	1.06	0.42	0.013	0.026	0.15	3.67	—
NICKEL-CHROMIUM STEELS.							
1	0.15	0.22	0.02	0.05	0.126	3.52	1.72
2	1.28	0.26	0.020	—	0.150	3.46	1.80
3	1.50	0.26	—	—	0.190	3.46	1.80

any temperature below 650° C. is different from the annealed state. It appears—and this is confirmed by the tempering-resistance curves—that at each temperature the steel attains a definite condition, retaining a certain amount of carbon in solution in the ferrite, and that this condition approaches closer to the annealed state, with progressive decrease in the amount of dissolved carbon, as the tempering temperature is raised. Between martensite and pearlite, two states—troostite and sorbite—are generally recognised; but it is clear that the transition from martensite to granular pearlite is progressive, and that troostite and sorbite are merely characteristic phases in the gradual change. Pearlite, sorbite, and troostite do not differ in state of division alone. They differ also in the amount of carbon in solution in the ferrite, and to this may be attributed the remarkable difference in their properties, which is commonly ascribed to state of division.

In conclusion, Mr. M. S. Fisher and Mr. J. M. Robertson wish to acknowledge their indebtedness for the research scholarships granted to them for two years by the Department of Scientific and Industrial Research.

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*The Structure of Thin Films. Part VII.—Critical Evaporation Phenomena at Low Compressions.*

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The measurements of compression and area on monomolecular films of fatty substances on water surfaces, described previously (1), were limited in accuracy by the disturbing effect of the jets of air necessary in the apparatus employed for measuring compression, for the purpose of preventing escape of the films past the barrier confining one end of the films. We think the error in measurements of compression with this apparatus may have been as large as half a dyne per centimetre in extreme cases, and as the apparatus was used under fairly accurately reproducible conditions, it was of the nature of a constant error. The reality of the lowest portion of the compression-area curves was therefore open to doubt.

We have now designed an apparatus in which the gap at the ends of the floating barrier is completely closed by very thin strips of gold ribbon, placed vertically in the water, and soldered to the ends of the float and to brass pieces pressed tightly against the sides of the trough. This arrangement can be made leak-proof and very sensitive. In order to measure the force on this float, at a given position, fine silk fibres connect the float to (a) an optical lever system consisting of a mirror suitably damped with an oil bath, mounted on a light torsion wire, which is in effect a practically frictionless bearing, and (b) a fine torsion wire provided with an accurately graduated divided head, whose divisions can be calibrated in absolute measure by hanging weights on a small balance mounted on the wire. Full details of the apparatus are given at the end of the paper.

Readings could be taken to 0.001 dyne per cm., but the accuracy obtainable was considerably less than this. The zero would keep constant to three or four thousandths of a dyne for a sufficient time to allow readings to be taken; but measurements of the compression of films were usually consistent only to about 0.01 or 0.02 dyne per cm. This is, however, an improvement of about fifty times, on the sensitivity of the previous apparatus.

Up to the present we have only been able to work at room temperature and in a cellar, since small vibrations and inequalities of temperature disturb

the position of the float. The effect of temperature has not therefore been measured with any accuracy; but since previous work has shown that the effect of lengthening the hydrocarbon chain of the molecules is almost exactly the same as that of lowering the temperature, we have been enabled to avoid this difficulty in great measure. Recent researches into crystal structure, as well as into the problems of capillarity, have shown abundantly what a powerful tool is the variation of the chemical constitution of organic substances, in a known manner, for the resolution of purely physical problems.

With this apparatus we have been able to trace, with films of substances practically insoluble in water, the course of the "critical phenomena" which were predicted by Langmuir (2) in his brilliant pioneer survey of the properties of films. These phenomena form a connecting link between the monomolecular films of soluble and of insoluble substances.

Figs. 1 to 4 show the results obtained on four homologous series, the fatty acids on  $N/_{100}$  HCl, and ethyl esters, nitriles, and alcohols on distilled water. The points are plotted in two curves, the compression  $F$  against the area  $A$ , and  $FA$  against  $F$ .

*Areas over 5000 sq. A.U.*

The curves all show that the pressure at large areas reaches the order of magnitude of what may be termed the theoretical "perfect gas" pressure, given by the equation,\*

$$Fa = 1.372 \times 10^{-16} T \quad (1)$$

or

$$FA = 1.372 T \quad (2)$$

( $F$  being the force in dynes per cm.,  $a$  the area per molecule in sq. cm., and  $A$  in sq. A.U.).

\* The theoretical basis of the equation  $Fa = RT$  (1) involves the following essentials (Langmuir (2); Schofield and Rideal (4)). For the equilibrium between a solute 2 in a solvent 1, and a surface film, Gibbs' adsorption equation governs

$$1/a = \Gamma_2 = dF/d\mu_2 = dF/RT d \log_e a_2. \quad (3)$$

$\Gamma_2$  is the adsorption in molecules per sq. cm.,  $R$  is  $1.372 \times 10^{-16}$ ,  $\mu_2$  and  $a_2$  the potential and activity of the solute. This depends only on thermodynamics and is exact in this form, by definition of activity and of potential.

Applying Langmuir's kinetic theory of adsorption (3), when the concentrations and adsorptions are small, the rate of condensation of molecules from the interior of the solution on the vacant spaces in the film is proportional to the concentration and activity in the solution; the vacant spaces being practically equal to the whole area of the surface, the rate of condensation on the film is proportional to  $a_2$ . In the dilute adsorbed film, the

The line  $FA = 396$ , corresponding to a temperature of  $15.5^\circ \text{C.}$ , is dotted in on each diagram.

molecules do not affect each other appreciably, therefore the average time of life of each molecule in the film is independent of the number present, and the rate at which the molecules leave the film for the interior is proportional to the number present, that is to  $\Gamma_2$ . The rate of condensation on the film being equal to the rate of leaving the film,  $\Gamma_2$  or  $1/a$  is proportional to  $a_2$ . Combining this with (3) we obtain easily  $Fa = RT$ .

To extend this reasoning to insoluble surface films, we make the assumption usually considered justifiable by statistical mechanics, that the immeasurably small concentration and activity have a definite numerical value.

Alternatively, we may apply the methods of kinetic theory to the motion of the molecules of an insoluble film in two dimensions.

Consider the molecules as points moving according to Maxwell's law in a plane. Let  $\Gamma_2$  be the number per sq. cm. The number of these which have velocity components, in two directions at right angles, between  $u$  and  $u + du$ ,  $v$  and  $v + dv$ , is

$$\Gamma_2 C e^{-hm(u^2+v^2)} du dv.$$

The total number of molecules of all velocities being  $\Gamma_2$ ,  $C$  is found to be  $hm/\pi$ .

The number of molecules of the above assigned velocities which hit a length  $dl$  of a straight boundary perpendicular to the direction  $u$ , in one second, is

$$\Gamma_2 u dl (hm/\pi) e^{-hm(u^2+v^2)} du dv,$$

and the change of momentum produced by these is

$$2\Gamma_2 u^2 m dl (hm/\pi) e^{-hm(u^2+v^2)} du dv.$$

Integrating over all positive values of  $u$  and all values of  $v$ , and substituting  $F dl$  for the total change of momentum per second on this element of the boundary,

$$\begin{aligned} F &= 2m\Gamma_2 \frac{hm}{\pi} \int_0^\infty u^2 e^{-hm u^2} du \int_{-\infty}^\infty e^{-hm v^2} dv \\ &= \frac{1}{2h} \Gamma_2 = RT\Gamma_2. \end{aligned}$$

Therefore  $Fa = RT$ .

This proof assumes that the molecules move in the film with average translational components of energy equal to  $\frac{1}{2} RT$ , and that this energy is wholly available for producing the pressure  $F$  on a barrier which is freely passed by water molecules but not passed at all by film molecules.

Experimental verification of the value of the constant in equation (1) cannot be made by the methods of Langmuir, and Rideal and Schofield, since the adsorption  $\Gamma_2$  is calculated from Gibbs' equation, which involves the correct value of  $R$ . The direct and independent measurement of the surface pressure and area of the insoluble surface films does appear to be a verification of the value of  $R$  for surface solutions, just as measurements of osmotic pressure in dilute solutions are a verification of  $R$  for solutions in three dimensions. In the light of our results, it is clear that Marcolin and Delaplace (6, 7) are mistaken in claiming that  $R$  for surface solutions is only a small fraction of the gas constant. We have not yet, however, worked with the actual substance with which most of their measurements were made.



Whether the experimental results can be said to approach exactly this value, or one somewhat lower, is perhaps doubtful. It is our experience that just with the very low pressures (at most 0.10 dynes per cm. in this region) the uncertainties of measurement become greatest. We have attempted to make specially careful experiments to determine the best value of  $FA$  at large areas, but could not reach an accurate conclusion. Indeed, the results

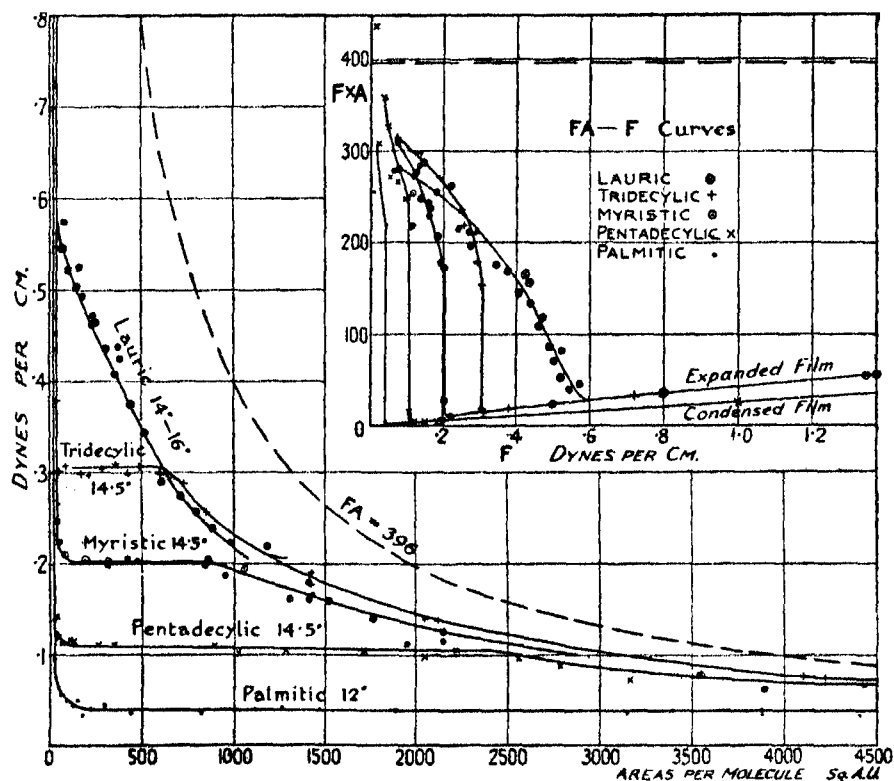


Fig. 1.

would vary in successive settings up of the apparatus, by an amount which was apparently slightly greater than the experimental error estimated from consideration of the errors which could arise from the contamination present and any spontaneous changes of zero. For instance, ethyl palmitate gave (mean of nine readings) 381 for  $FA$ ; palmitic nitrile (4), 309; myristic nitrile (4), 376; ethyl margarate (6), 499; ethyl pentadecylate (4), 344; myristic acid (9), 280. All of these were typical results, except ethyl margarate; but

on one particular day, a large number of readings were taken and all were lower, actually about the lowest recorded in three months. These were, ethyl pentadecylate, 167; myristic nitrile, 146; palmitic nitrile, 156. It is possible that on this day the apparatus was reading consistently about two-hundredths of a dyne low, as an observation was also made on ethyl pentadecylate at smaller areas, and the pressure was about this amount below the

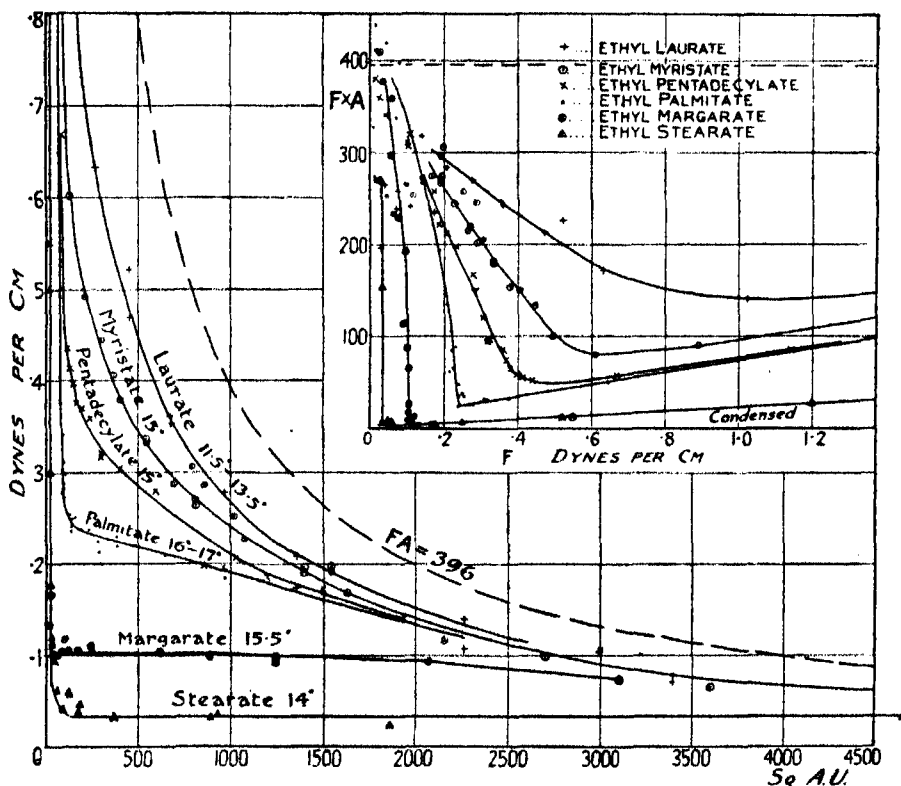


FIG. 2.

pressure obtained from very numerous previous experiments with this substance. It is just possible that there is some detail in setting up the instrument, which we may have overlooked, which may cause the zero to shift slightly during the spreading of the film.

The results support the conclusion that the product  $FA$  increases, with increasing area, to a limit close to  $1.372 T$ , and not more than 25 per cent. below this value.

*Areas below 5000 A.U.*

Between 5000 A.U. and the areas at which the films are expanded or condensed, as described in previous papers, the curves of all the substances resemble closely the isothermals of vapours near their critical point. There is a horizontal vapour pressure region, except where the substance is above the critical point. This is shorter as the length of chain is shortened in each

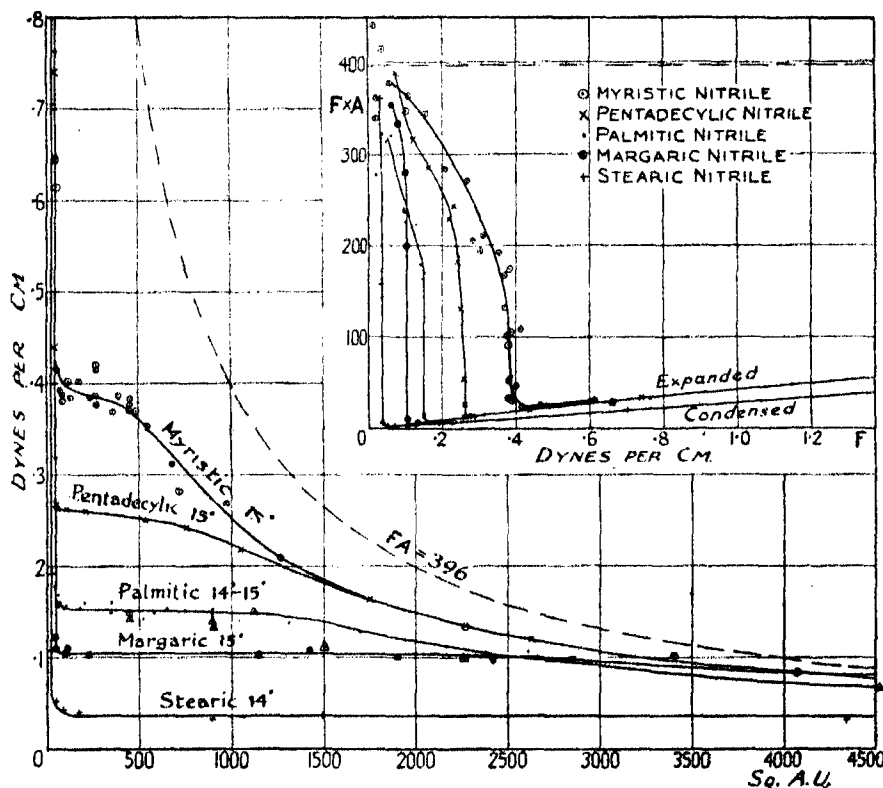


FIG. 3.

homologous series, and this shortening is analogous to the effect of rising temperature in shortening the length of the vapour pressure region in the isothermals of a single substance.

Since it has been shown in previous papers that the lengthening of the hydrocarbon chain by one carbon atom has almost exactly the same effect as lowering the temperature by  $10^\circ$ , in the vicinity of room temperature; and since the difference in vapour pressure between successive members of the fatty acid series is about 0.1 dyne per cm., between 0.1 and 0.3 dyne per cm.,

we conclude that a rise of temperature of  $1^{\circ}\text{C}$ . increases the vapour pressure of pentadecylic and myristic acids by about 0.01 dyne per cm. In one or two instances, while working with the same substance on different days, we have been able to obtain actual measurements of the vapour pressure at temperatures differing by about  $3^{\circ}$ ; these confirmed the conclusion that the vapour of these substances is raised about 0.01 for  $1^{\circ}$  rise of temperature.

It is evident that the curves corresponding to the "condensed films," and

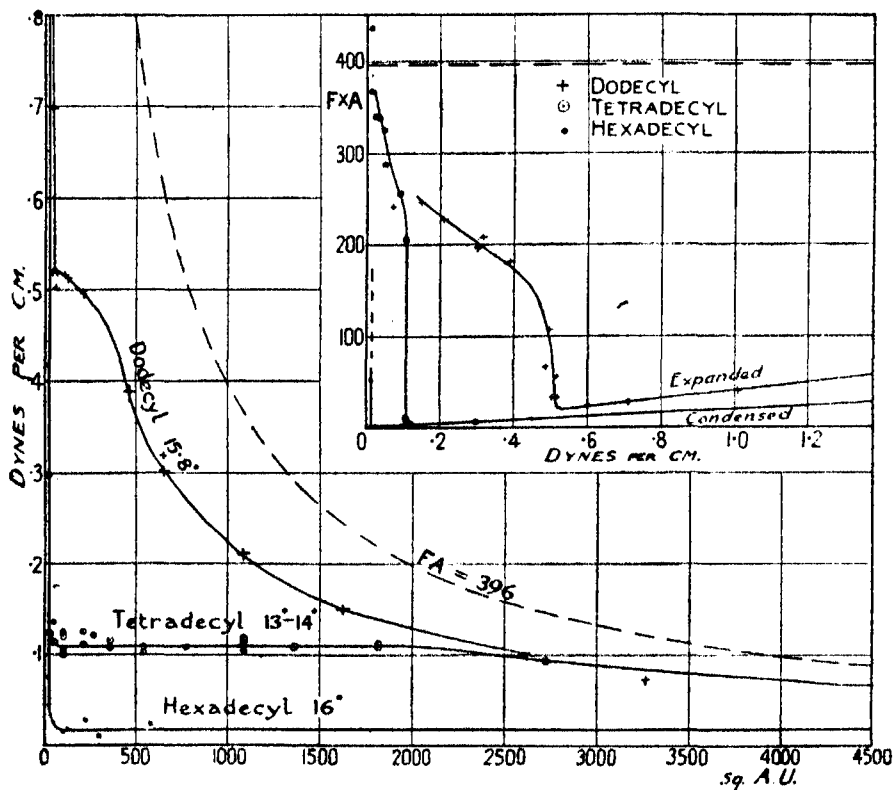


FIG. 4.

also the majority of those to which the name "expanded films" was given in previous papers, behave as liquids (or solids) in their tendency to evaporate in two dimensions. The hypothesis advanced in Part III, that the expanded films are gases, must be abandoned; at the best it was never more than a superficial analogy, as the pressures in the expanded films are so much less than the theoretical perfect gas pressures.\*

\* Mr. Schofield pointed out to us, early this year, the conclusive nature of the evidence from the FA-F curves on previously published results, that the expanded films are analogous to liquids, not gases.

At the left hand end, the horizontal or "vapour pressure" region passes fairly abruptly into the condensed or expanded films. Such rounding off of the angle between these curves as has been found may be due either to experimental error, or possibly to a very slow attainment of equilibrium between the two-dimensional liquid and vapour, when the amount of vapour is small. In one or two instances there was an unaccountable irregularity in successive measurements of pressure, just at the area where the "liquid" curve joins the "vapour pressure" curve; this might amount to six-hundredths of a dyne in extreme cases, and with tetradecyl alcohol we found a number of films which appeared in this region to have a vapour pressure some two-hundredths of a dyne too low.

Table I gives the vapour pressures, and the approximate areas at the right hand end of the vapour pressure curves.

Table I.—Evaporation in Two Dimensions.

Substance.	Temperature, C.	Approximate area at end of horizontal portion. Sq. A.U.	Vapour pressure dynes per cm.
Lauric acid .....	14—16	above critical point	
Tridecyl acid .....	14·5	550	0·308
Myristic acid .....	14·5	850	0·203
Pentadecyl acid .....	14·5	2400	0·108
Palmitic acid .....	12	5500	0·039
Dodecyl alcohol .....	15·8	above critical point	
Tetradecyl alcohol .....	13—14	1950	0·110
Hexadecyl alcohol .....	16	(5000)	0·018
Ethyl laurate .....	11·5—13·5	above critical point	
Ethyl myristate .....	15	"	"
Ethyl pentadecylate .....	15	"	"
Ethyl palmitate .....	16—17	"	"
Ethyl margarate .....	15·5	(1000)	0·103
Ethyl stearate .....	14	(6000)	0·033
Myristic nitrile .....	15	above critical point	
Pentadecyl nitrile*	15	—	(0·26)
Palmitic nitrile*	14—15	(1000)	0·15
Margaric nitrile .....	15	2200	0·105
Stearic nitrile .....	14	(10,000)	0·036

\* There is a little doubt about the results on palmitic and pentadecyl nitriles. The palmitic had been prepared from a good specimen of the acid, and purified by two distillations, once through a good fractionating column. At this stage, it was found that the best line which could be drawn through the points sloped slightly downwards, from 0·153 at 100 sq. A.U. to 0·149 at 1000 A.U. The specimen was then further purified by redistillation and five recrystallisations, but there still appeared to be a slight slope downwards in the curve. Whether this is genuine or no it is scarcely possible to say, and since the pentadecyl nitrile was almost certainly not pure, and too small in amount for further purification, it gives no help in determining whether or no palmitic nitrile was above or below its two-dimensional critical point. However the curve for myristic nitrile—of very fair purity—resembles so closely that for a gas or a film very near the critical point, that we think it most likely the palmitic nitrile is well below the critical point.

The measurements of area at the end of the horizontal region depend on the detection of differences of pressure much smaller than 0.01 dyne, and are therefore subject to very large errors. Their order of magnitude is however important, as by their aid the free and total energy changes of the two-dimensional evaporation process may be calculated approximately. If  $F_p$  is the vapour pressure, then the free energy change is  $F_p (a_1 - a_2)$ , and the latent heat, by the Clausius-Clapeyron equation, is  $T \frac{dF_p}{dT} (a_1 - a_2)$ ,  $a_1 - a_2$  being the difference in area at the two ends of the horizontal portion of the curves. The values of  $a_1 - a_2$  are for tridecylic acid about  $500 \times 10^{-16}$  sq. cm., for myristic 800, for pentadecylic 2300.

From the curves, the increase in vapour pressure at constant temperature for a decrease in the length of the chain of one carbon atom is 0.1 dyne nearly; since this difference in length of chain corresponds to a temperature difference of nearly  $10^\circ$  (see Parts III and V),  $dF_p/dT$  is 0.01 dyne per cm. per degree. Hence the order of magnitude of the free and total energies of the evaporation is:—

—	Free energy change.		Latent heat.	
	Ergs per molecule.	Calories per gram molecule.	Ergs per molecule.	Calories per gram molecule.
Tridecylic acid .....	$150 \times 10^{-16}$	220	$1390 \times 10^{-16}$	2000
Myristic acid .....	160 ..	230	2200 ..	3200
Pentadecylic acid ....	250 ..	360	6500 ..	9500

It is evident from the large values for the latent heats, and the great difference between these and the free energy changes, that there is a considerable cohesion between the molecules in the expanded films. Actually the latent heats are of the same order of magnitude as those for the spreading of stearic acid from the bulk solid to a condensed film (Cary and Rideal, 5, p. 329). "Cohesion," however, in the films, may not have exactly the same meaning as in gas, since the film molecules are lying on, and to some extent among the water molecules; and their relation to the water molecules may not be thermo-dynamically the same in the "expanded" as in the "gaseous" state of the films.

#### *The Structure of Gaseous and Expanded Films.*

Our results give no information on the structure of the gaseous films, except that the molecules are confined to the surface, and move about nearly independently of each other, cohesive forces between them being small. Their

motions are, of course, determined by the Brownian motion of the water molecules, and the average translational kinetic energy in each component is  $\frac{1}{2}RT$ . The films in this condition seem to be a continuous series with, and to have the same properties as, the films of soluble substances adsorbed at a surface. Langmuir (2, p. 1887) shows that as the length of the chain of a soluble fatty acid molecule is increased, the potential energy change accompanying the adsorption of equal numbers of molecules increases by a constant amount per carbon atom; he concludes that each  $\text{CH}_2$  group added occupies the same position on the surface as those already there, and consequently that the chains lie flat on the surface. Presumably, with the insoluble films, the molecules in the gaseous condition also lie out flat on the surface, at least for some part of their time. The evidence would be more complete if measurements on the adsorption were available for acids between six and twelve carbons in length; it is to be hoped that accurate measurements on the surface tension of solutions of these acids, and of their derivatives, will soon be forthcoming.

The expanded films tend towards a definite maximum area at no compression. This is clearly shown by figs. 1 to 4, and is indicated by the pressure-area curves previously published by Langmuir and by one of us, as well as by Rideal and Cary's experiments on the spreading of films from a mass on the surface (5). In the case of those films which are below the critical evaporation temperature, the course of the expanded film can be actually traced down to a few tenths of a dyne per cm., before evaporation commences. The area at no compression is of the order 45–50 sq. A.U. This is too small for the molecules to be lying flat, and not overlapping. It is not constant for different homologous series, and may possibly vary within each series slightly, in the direction of smaller areas for longer chains. This is not yet certain, however.

None of the probable static arrangements of the molecules appears to provide an explanation for all the properties of the expanded films. We are obtaining further data on their properties with an apparatus similar to that of this paper, but with a thicker torsion wire and less sensitivity. In recent experiments the addition of an oxidising agent, which acts on the ethylenic linkage, to the water, has a strong effect in changing a film from condensed to expanded, when the molecules have an ethylenic linkage in the middle of the chain; but no effect if the chains are saturated. It appears that increasing the attraction of the water for the chains tends to expand the films.

The definite limit to the area points to the molecules within the expanded films being always within the range of attraction of their neighbours.

The condensed films pass into the expanded films on raising the temperature.

It is not improbable that the molecules in the expanded films have lost their orientation and are in constant agitation, possibly passing through horizontal and vertical positions. When melting occurs in three dimensions, no great change of *volume* accompanies the loss of definite orientation of the molecules, since any oriented layer in a crystal which increases in area in its own plane would decrease in thickness by an amount probably sufficient to keep the volume approximately constant. But any loss of the vertical orientation in a two-dimensional film of long-chain molecules must be accompanied by an increase in area. The process of expansion of a condensed film thus appears to be analogous to *melting*, a term which one of us applied to the phenomenon when first meeting with it (Part I, p. 348).

The films differ from three dimensional matter, in that melting may occur in more than one stage, the different stages taking place at different temperatures. Thus, with hexadecyl and octadecyl acetamides the films were shown (Part VI) to lose the two-dimensional rigidity which prevents the motion of dust particles lying on the surface, at a definite temperature which is about  $12^{\circ}$  below the temperature of expansion. Below this temperature the molecules were interlocked so that they could not rotate about a vertical axis on the surface, and at this temperature freedom of movement in the plane of the film commenced, probably by the removal of the restraint on rotation. The change was particularly noticeable with these substances, as a slight increase of area occurred simultaneously with the loss of rigidity; the increase of area was, however, so small, that it is improbable that the vertical orientation of the molecules was appreciably impaired. In Part VI the mistake was made, when describing the effect of temperature on the films, of regarding the expanded films as the vapour phase.

We can see very little evidence for Cary and Rideal's suggestion (5, p. 326) that the expansion is a gradual hydration of the molecules in the film, the heads thereby becoming so much larger as to force the molecules apart. There appears to be no collateral evidence for hydration of the polar groups of molecules, in any other state of matter, regularly increasing from a negligible amount to a final value in a range of only a few degrees as the temperature rises. Neither is it easy to account for the much greater compressibility of the expanded films, which can be compressed into an area little greater than the condensed films, by supposing the molecules are carrying a load of attached water molecules. The equation of state proposed by these authors for the expanded films (p. 309) does not fit direct measurements of pressure and area, the divergence being greatest at fairly low pressures. We have not an alter-



native equation to propose at present, but are continuing work on this very interesting state of matter.

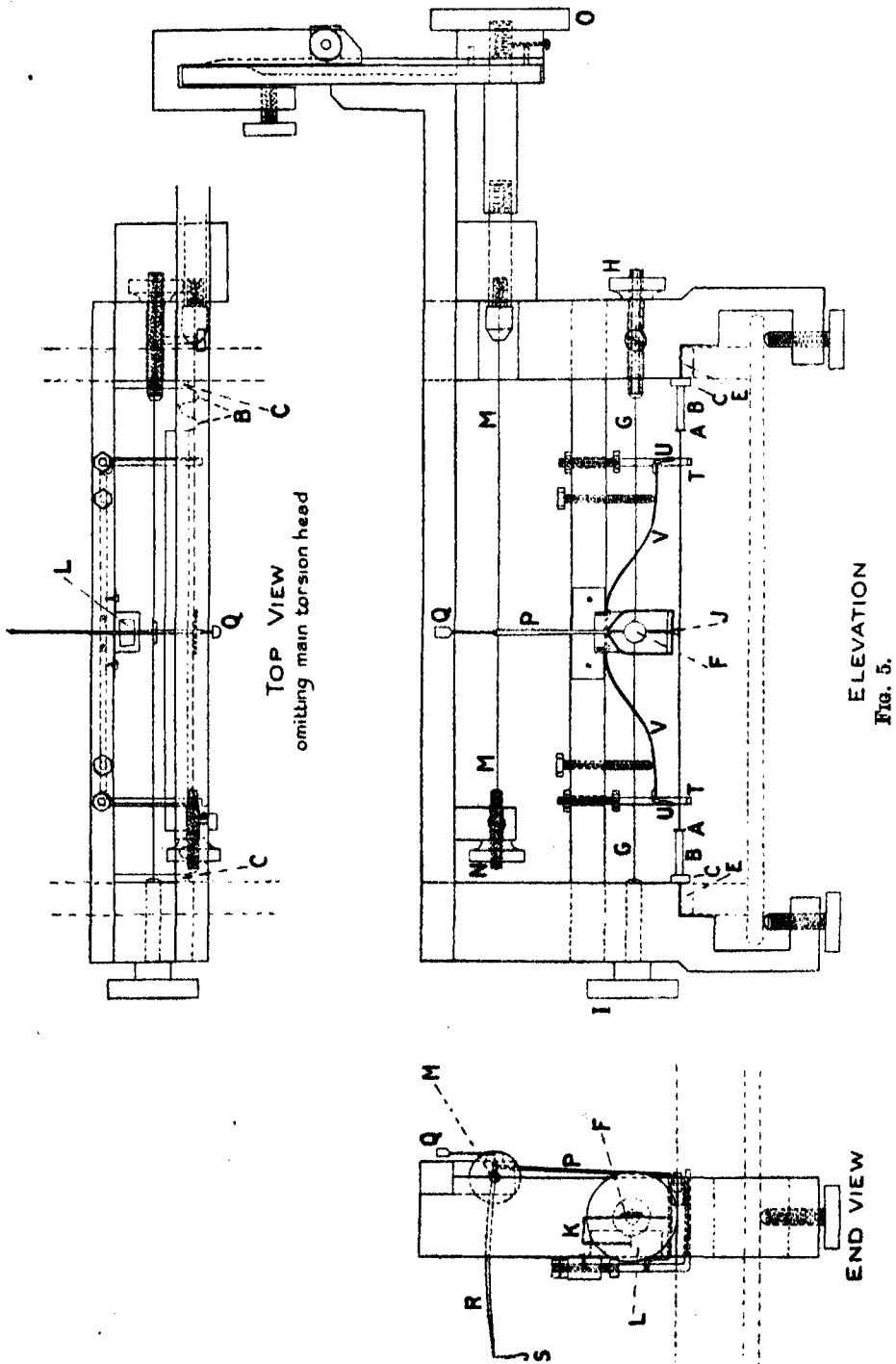
*Description of apparatus.*

Fig. 5 is a drawing, and figs. 6 and 7 are photographs, of the apparatus in position on the trough. The same brass trough was used as in previous work. The float AA is of copper foil 11.04 cm. long. The ends carry small vertical strips of copper to which are soldered strips of gold ribbon B, 2 mm. wide and about 0.009 mm. thick, bent into a  $\sim$  shape, and fixed with the width perpendicular to the water surface. The other ends of the strips are soldered to brass pieces CC, which form part of the frame of the apparatus. The distance between the two pieces CC is 13.66 cm. A tight fit between the pieces CC and the inside edge of the trough was obtained by letting into the top of the trough movable but tightly fitting pieces of brass EE, which were bevelled to an angle of about  $80^\circ$ , the sharp edge being pressed tightly up against the pieces CC. The apparatus was fixed about 11 cm. from the end of the trough.

The mirror F indicating the position of the float is carried in a very light holder on the torsion wire GG, of phosphor bronze, about 0.08 mm. diameter. The holder carries two light projections, one coming down close to the float; the other, K, going up, and bent back twice at right angles, ending in a flat plate which moves in a small oil bath L.\* A silk fibre is cemented on to the first of these projections and to a lug J in the middle of the float AA. The head I and the nut H admits of varying the torsion and the tension on the wire GG.

The upper torsion wire MM, of phosphor bronze about 0.12 mm. diameter, is controlled by a head O which carries a vernier arm moving over a scale of  $180^\circ$  and reading to  $1/50^\circ$ . A clamping arrangement and slow motion screw, similar to those found on high grade polarimeters, are provided. The scale was graduated by Messrs. Elliott Bros.; its attachments, as well as many other details of the frame, were partly designed and very ably made by Mr. C. E. Stewart, in this laboratory. The axis was made in screwed sections to permit easy changing of the torsion wire. The tension of this wire is regulated by the nut N, which draws a screwed rod carrying the end of the wire through a hole in which it cannot turn. The "microbalance" PQMRS is soldered on the wire

\* The oil used was the residue left after distilling off the lighter fractions from medicinal paraffin up to  $250^\circ\text{C}$ . at 1 mm. pressure. Its viscosity was about the same as that of a thick "air cooled" motor oil, which would be equally suitable, but for the risk of contamination from traces reaching the water.



at the middle of the apparatus. It is a framework of nickel silver, with a stirrup at the lower end of the vertical arm P ; this comes nearly to the water surface and is joined to the lug J on the float by a silk fibre. Q is a counterpoise

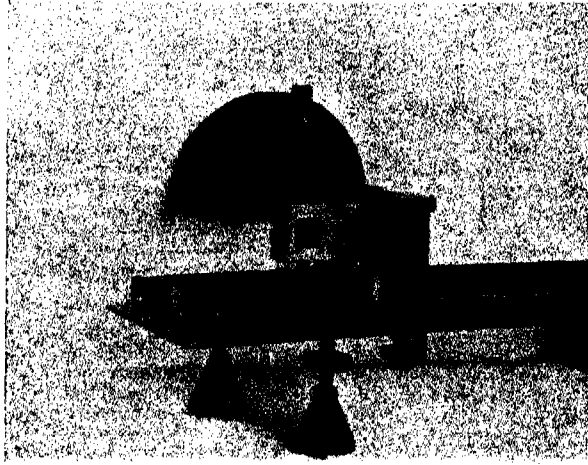


FIG. 6.

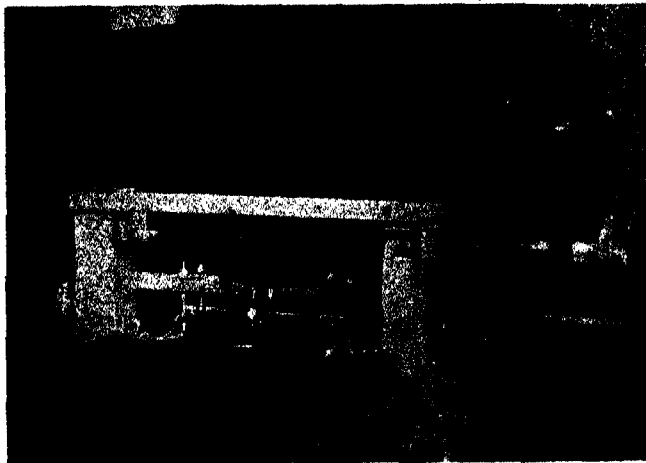


FIG. 7.

adjusted so as to bring the centre of gravity near to the torsion wire ; the end of R is sharpened, and a hook S hung by a silk fibre over the sharpened end, the fibre being cemented a short distance along the beam. The lines joining

the ends of the arms P and R were at right angles. The lengths of the horizontal and vertical arms were measured by a reading microscope and were respectively 5.065 and 4.875 cm. In calculating the force exerted by the film on the float, which is balanced by the torsion of MM, transmitted through the arms of the "microbalance," we assume that, of the pressure exerted against the two gaps at the ends of the float, blocked by the gold ribbon springs, half is borne by the float and half by the fixed supports on the frame. The effective length of the float is therefore its actual length plus half the length of the gaps, or 12.35 cm. A weight of 10 mg. on the hook S is equivalent to 0.8255 dyne per cm. In repeated calibrations extending throughout the work, the distance through which the torsion head had to be turned to compensate a weight of 10 mg. never differed by as much as 1 per cent. from  $27.9^\circ$ . Hence  $1^\circ$  on the torsion head is, with this wire, equal to a pressure of 0.0296 dyne per cm. Hooke's law was obeyed over the range of the scale, within 1 per cent.

The apparatus was nearly always used by first adjusting the spot of light from the mirror to zero on a scale, by means of the torsion head, then putting on a film at a known area and re-adjusting by means of the head; the difference in readings on the head giving the pressure. On occasion, for small pressures the torsion head was not touched, and actual excursions of the spot of light on the scale observed. The scale was calibrated directly in this case, by small weights on the hook. Rider weights calibrated at the National Physical Laboratory were used as standards.

A clamping arrangement for the float is necessary to prevent damage when the apparatus is off the trough. Two brass supports, TT, can be raised up to the float and brass pieces, UU, fastened to the ends of a spring VV, lowered on to it by screws passing through a transverse brass bar at the back of the frame, and operated from outside the covers of the apparatus.

Light sheet aluminium covers, with windows of thin glass where necessary, were fitted to front and rear of the apparatus to exclude draughts. Uncontrollable variations of zero were very much diminished by these covers. A sliding door was provided to permit the hanging of weights on the hook. The photograph fig. 6 shows the apparatus from the rear with covers on, fig. 7 from the front with covers off.

#### *Details of Cleaning and Use.*

The trough is cleaned as before, with emery cloth under running water; then dried with plenty of *boiling* water, which brings the trough to such a temperature that on painting with a benzene solution of paraffin wax, the

benzene is rapidly evaporated and the paraffin remains molten for a time on the surface. A much more durable and efficient coat of wax is deposited in this way than if the trough is only got warm before paraffining. Ordinary commercial high melting paraffin wax was quite satisfactory, and scarcely contaminated the surface at all. Occasionally a recrystallised specimen was used with little, if any, advantage.

The pressure-measuring apparatus is washed with clean toluene, and the following parts paraffined with a benzene solution of wax: float AA, upper half of the gold ribbons BB, and upper half of the brass pieces CC. The recess in the frame into which the sides of the trough fit is also paraffined, but a strip a few millimetres wide nearest the water is left bare.

It is necessary to test the apparatus for leaks. These may occur at the ends of the float at the junction with the gold ribbons, or at the other end of the gold ribbons where they join the brass pieces CC, and may be detected, unless very small, by placing a very little talc on the surface. Such leaks may usually be stopped by pushing the gold ribbons down into the water two or three times.

To measure the length of the film we have used a scale held in a clamp above the trough. The cover in front of the apparatus prevents the scale being continued to the zero mark. An extension piece is used for setting the scale in position after the apparatus is clamped on the trough, but before the front cover is put on.

The water surface is cleaned with paraffined glass barriers several times. The disturbance settles down in a minute. The torsion head is adjusted to bring the spot of light to zero, and the film is put on from a very fine calibrated dropping pipette. It is generally possible to obtain a steady reading of pressure within one minute after putting on the film.

The choice of solvent for measurements at these low pressures is important. It was found that benzene and toluene, carefully purified by distillation, and in one case also by treatment with silica gel to adsorb any possible remaining non-volatile impurities, apparently did not evaporate quite completely in a reasonable time, but left a detectable pressure behind on the apparent surface. This was probably due, not to non-volatile impurities, but to the slight solubility of these solvents in water. A small amount probably penetrates into the water during spreading, and evaporates slowly thereafter, the molecules present at any instant in the surface causing a pressure. Petroleum ether of b.p. 60–70° is practically free from this objection; this solvent has been used for all the measurements recorded in this paper. Three or four drops.

would cause a residual pressure at most three-thousandths of a dyne, after two minutes. We observed that when 10 per cent. of alcohol was added to the petroleum ether the residual pressure from the solvent was very considerable for a long time; this confirms the view that it is important to use solvents which are practically insoluble in water.

Most of the points in figs. 1 to 4 were determined by single observations on separate films, the barrier being set and the number of drops and strength of solution chosen so as to give the required area. This was the most accurate, though a slow, method of obtaining results. Any residual errors due to traces of solvent were shown to be negligible, by using solutions of various strengths, *e.g.*, a given area was frequently obtained by using one drop of a stronger solution, and with 10 drops of the solution diluted 10 times. With a clean trough not much difference was made to the results if the film was put on at a large area and the barrier moved up to successive positions. We have also determined the curves, in the course of developing the final design of the apparatus, with benzene and toluene as solvents; and with a preliminary apparatus which employed the float with metal ribbon at the ends, but measured the forces by means of the balance used in previous work, the vertical arms of this passing through holes in the float. The results obtained in these various ways are not recorded here, being slightly less trustworthy than those with the final apparatus; but the curves are very nearly identical with those presented. The apparatus with a balance for measuring forces was far more troublesome than that with torsion wires.

The amount of contamination was estimated by reducing the area of the supposed clean surface of water to one quarter, by moving the barrier. On a freshly cleaned trough this increase of pressure was not more than 0.03, and was sometimes 0.02 dyne per cm. If we may assume that the contamination behaves nearly as a perfect gas, the contamination before reducing the area would be less than one-hundredth of a dyne. This would have to be subtracted from both the zero and the final readings of the torsion head, and would only affect the results by increasing the total pressure of the film by about 0.01 dyne, thus bringing the film a trifle nearer to the pressure at which the departures from the perfect gas law become large. For the purposes of this paper, this contamination appears to be negligible.

It is generally possible to use a trough for successive experiments over two or three days, before the contamination is doubled in amount. At this stage the apparatus has been dismantled and cleaned, when accurate results have been required.

*Preparation of Materials.*

The substances used, or the methods of preparation, have been the same in this work as previously. The pentadecylic and margaric nitriles were prepared from the iodides with one fewer carbon atom in the chain, by boiling with alcoholic potassium cyanide (8). Their purity was tested by hydrolysing to the acids and taking mixed melting points with known good specimens of the acids. The margaric nitrile was pure, but owing to accidents resulting in loss of material in the preparation of pentadecylic nitrile this specimen was not pure. We should expect impurity to be shown by a slope in the vapour pressure region of the curves, and it is satisfactory to find very few specimens which gave a detectable slope.

Dr. W. E. Garner has most kindly given us specimens of the fatty acids which he has purified himself, and the results on these were not seriously different from those on our own specimens.

*Summary.*

By means of a new apparatus, measurements of the surface pressure of monomolecular films have been made at room temperature, down to 0.01 dyne per cm.

At areas greater than about 5000 square A.U. per molecule, the pressures exerted by films of insoluble fatty substances tend to a value within 25 per cent. of that given by the equation  $Fa = RT$ ,  $R$  having the same value as in a perfect gas. The experimental difficulties of measurement at these areas are so great that it is probable that the divergences from the theoretical values are within experimental error.

Between 100 and 5000 square A.U. the pressure-area isothermals closely resemble those for liquid and vapour in three dimensions. With longer chains in the molecule there is a horizontal "vapour pressure" region, ending on the one hand in an imperfect gaseous film, on the other, in either the condensed or the expanded type of film. When the chains are shorter, a condition which corresponds to a higher temperature, the "vapour pressure" region disappears, and the films are above their "critical point."

Expanded films are analogous to liquids, not vapours, and there is considerable cohesion between the molecules in them. The heats of two dimensional evaporation from expanded to gaseous films are of the same order of magnitude as the heats of spreading, from bulk to a condensed film, on a water surface. The evidence, though incomplete, indicates loss of orientation in expanded films.

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*Note on the Spreading of Solids on Water Surfaces.*

By N. K. ADAM and G. JESSOP.

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Cary and Rideal (1), in their recent excellent studies of spreading of solid and liquid substances on water, show that the rate of passage of molecules from a crystal of myristic acid, into a film on the surface, is proportional at any moment to  $F_c - F$ , where  $F$  is the compression in the film and  $F_c$  the compression at which the film is in equilibrium with the crystal and no more spreading occurs. Experimentally they could detect no compression until enough had spread to cover the whole available surface with a film packed to the density of an expanded film at no compression—about 46 Å.U.

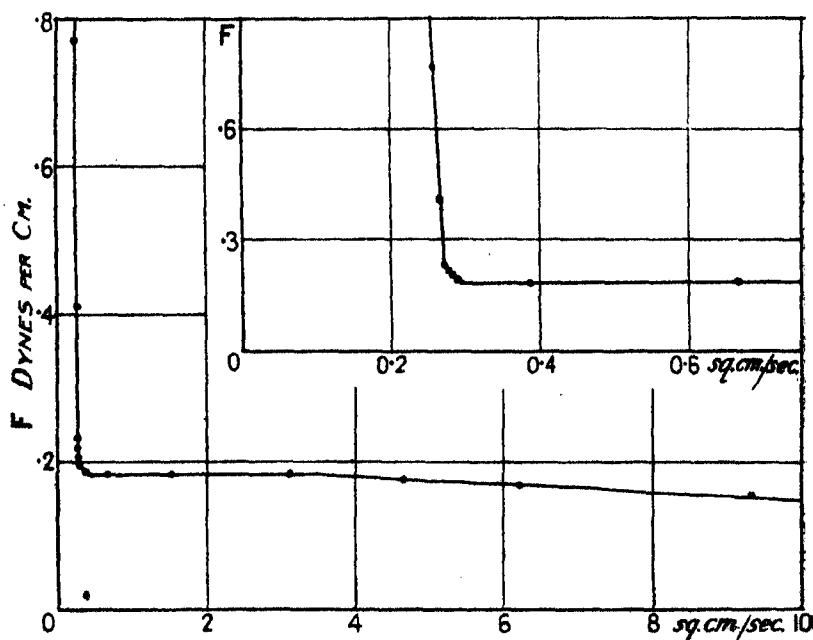
Probably their measurements were not sufficiently accurate to detect a compression much less than 0.5 dynes per cm., if this persisted for a long time. But if their theory, which agrees well with the views on spreading of one of us (2), is correct, a small compression should be set up very soon after the crystal is placed in the surface, and this should rise to, and remain constant at, the "two-dimensional vapour pressure" of myristic acid, for some time, before the spread film has reached the density of the expanded film. In this region  $F$  is negligible compared with  $F_c$ , hence the rate of spreading from the crystal is constant.

We have tested this point, with the apparatus recently described (3) for the measurement of low compressions, using an area on the trough of 280 sq.cm. A glass rod coated with the solid acid, of measured diameter, was placed vertically in the trough at various positions. The position was found to have no appreciable influence on the results. The pressure reached 0.1 dyne per cm. in



10 seconds. In  $1\frac{1}{2}$  minutes it had reached 0.185 dynes, and remained constant at this for about 14 minutes longer. Then it rose slowly for two or three minutes, and at  $18\frac{1}{2}$  minutes rose very rapidly. This rapid rise corresponds to the first depression of surface tension observed by Cary and Rideal.

Plotting the area of the surface, multiplied by the *reciprocal* of the time, as abscissæ, against the compression, a curve should be obtained in which the abscissæ are proportional to the area per molecule in the film, on the assumption that the rate of equalisation of pressure in the film is very great compared with the rate of spreading from the crystal. This has been done in the figure,



Spreading of Myristic Acid. Initial Stages.

the curve being practically identical with the  $F$ - $A$  isothermal for myristic acid on  $N/100$   $HCl$ . The upper curve is on a larger horizontal scale than the lower, and shows accurately the point at which the nearly vertical curve of the expanded film cuts the horizontal line of the vapour pressure. This occurs at 0.273 sq. cm./sec. The circumference of the rod was 1.325 cm., the area 280 sq. cm. From a recent careful experiment the area per molecule at this point on the isothermals is 46 A.U. within 3 per cent. Hence the rate at which the molecules left the rod was  $4.5 \times 10^{18}$  molecules per second per centimetre of circumference. This is considerably smaller than that found by Cary and

Rideal at  $25^\circ$ ; but our temperature was  $15.8^\circ$ , and it would be possible to extrapolate their curve (p. 311) to agree with this determination.

*Summary.*

Cary and Rideal's observations on the spreading of myristic acid on water have been continued down to very low compressions. A small pressure, that of the "gaseous" state of the films, is set up within a few seconds after the crystal touches the surface, and the "two dimensional vapour pressure" very soon afterwards.

REFERENCES.

- (1) Cary and Rideal, 'Roy. Soc. Proc.,' A, vol. 109, pp. 306-312 (1925).
- (2) Adam, 'Nature,' vol. 115, p. 512 (1925).
- (3) Adam and Jessop, 'Roy. Soc. Proc.,' A, *supra*, p. 434.

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*Structure of  $\alpha$  Quartz.*

By REGINALD E. GIBBS, M.Sc.

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As soon as the structure of  $\beta$  quartz (these Proceedings, A, vol. 109, Sir William Bragg and R. E. Gibbs) was known, it was natural to reconsider that of the  $\alpha$  variety and attempt to narrow down the range of uncertainty which existed. The general properties of both varieties of quartz have been dealt with fully in the paper mentioned above, and to avoid repetition it will be necessary to refer to it frequently.

In that paper it was shown that the lowering of symmetry from  $\beta$  to  $\alpha$  quartz introduced three extra unknown parameters, making four in all, a statement which sums up the whole difficulty of the determination of the  $\alpha$  quartz structure. No guiding principle can be introduced simultaneously to aid in its solution, and one is left as before, with intensity measurements alone, to settle not one, but four parameters. However, all the physical properties of quartz suggest that there is but a small change at the transition temperature, and therefore it may be tentatively supposed that no very drastic alteration occurs in the structure.

Attacking the problem experimentally, the lack of hexagonal symmetry was studied by obtaining oscillation photographs in which the zones containing

planes such as  $110\bar{1}$  were separated from those containing such as  $10\bar{1}1$ , etc. This was necessary because when the crystal was completely rotated about the  $c$  axis the reflections from these two zones containing planes of equal spacing but of different reflecting power were superimposed; this was overcome by taking oscillation photographs for which the crystal was rotated backwards and forwards about the same axis through an angular range only just sufficient to include reflections from planes the comparison of which was required. These photographs showed important differences between the  $1\bar{1}03$  and the  $10\bar{1}3$  planes together with smaller changes for a few others. Several Laue photographs were taken which also showed variations between corresponding planes. Notably the following results were obtained :—

$\bar{1}011$ weak.	$\bar{1}101$ strong.
$\bar{3}031$ missing.	$\bar{3}301$ strong.
$\bar{5}052$ strong.	$\bar{5}502$ missing.
$\bar{5}231$ missing.	$\bar{5}321$ medium.
$\bar{5}141$ very weak.	$\bar{5}411$ weak.
$\bar{4}312$ strong.	$\bar{4}132$ weak.

The zone whose axis was the pyramid edge containing the planes  $2111$ ,  $\bar{3}121$ , the signal face  $s$ , etc., was stronger than the corresponding one containing the planes  $1\bar{2}11$ ,  $1\bar{3}21$ . The Laue photographs given by Jaeger and Haga (Proc. Amster. Acad., 1916) were also studied and numerous other inequalities recorded.

In order to obtain a more quantitative record of these important planes, measurements of their intensities were made on an ionisation spectrometer. Some of the results may be stated briefly as follows :—

$10\bar{1}0$ :	$10\bar{1}1$ =	55 : 195
$10\bar{1}1$ :	$20\bar{2}2$ =	195 : 30
$01\bar{1}1$ :	$02\bar{2}2$ =	105 : 12
$10\bar{1}1$ :	$01\bar{1}1$ =	195 : 105
$20\bar{2}3$ :	$02\bar{2}3$ =	21 : 42
$30\bar{3}2$ :	$03\bar{3}2$ =	22 : 15
$40\bar{4}3$ :	$04\bar{4}3$ =	5 : 7
$10\bar{1}2$ :	$01\bar{1}2$ =	12 : 24
$20\bar{2}4$ :	$02\bar{2}4$ =	Missing.
$20\bar{2}1$ :	$02\bar{2}1$ =	7 : 17
$10\bar{1}3$ :	$01\bar{1}3$ =	15 : ?
$20\bar{2}6$ :	=	Missing.
$30\bar{3}1$ :	$03\bar{3}1$ =	37 : ?

These confirm the results previously obtained photographically and a few may be considered with special interest. It has already been pointed out (these Proceedings, vol. 107) that in the  $\alpha$  quartz the oxygen atoms cannot lie in the same plane perpendicular to the  $c$  axis as the silicons, and here the existence of a difference of intensity between the planes  $20\bar{2}3$ ,  $10\bar{1}3$  and the corresponding planes  $02\bar{2}3$ ,  $01\bar{1}3$ , demonstrates the necessity of a movement of the oxygen atoms out of the planes perpendicular to the  $c$  axis which they occupy in the  $\beta$  structure. This may be seen in the following way, the diagram fig. 1 is a projection of this structure on a plane parallel to the  $c$  axis and perpendicular to the side of the cell so that the planes  $m\bar{m}on$  are perpendicular to the plane of the paper. The unit pattern is selected to possess centro-symmetry as this simplifies subsequent calculations. In the transition from  $\beta$  to  $\alpha$  quartz,

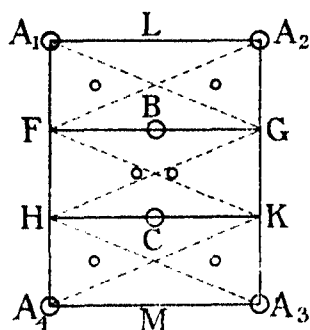


FIG. 1.

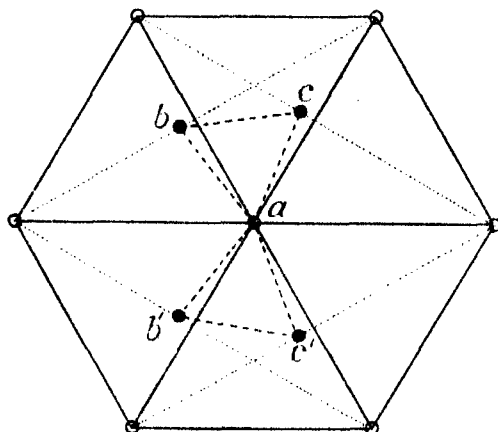


FIG. 2.

symmetry conditions constrain the silicon atoms B and C to move along horizontal lines FG and HK by equal distances in opposite directions, so that any movement on their part would affect the planes  $A_2F$ ,  $GH$ ,  $KA_4$  and  $A_1G$ ,  $FK$ ,  $HA_3$ , i.e.,  $10\bar{1}3$  and  $01\bar{1}3$ , equally. Exactly similar remarks apply also to the planes  $LF$ ,  $A_3H$ ,  $GA_4$ ,  $KM$  and  $LG$ ,  $A_1K$ ,  $FA_3$ ,  $HM$ , i.e.  $20\bar{2}3$  and  $02\bar{2}3$ , in fact to any pair of planes of this type that intersect on the lines FG and HK, e.g.  $40\bar{4}3$  and  $04\bar{4}3$ . These intensity differences cannot be due to either silicon or oxygen movement perpendicular to the  $c$  axis, but must arise from movements of the oxygen atoms out of the basal planes occupied in the  $\beta$  state. Next it will be noted that whereas  $\bar{3}301$  is a much stronger reflecting plane than  $\bar{3}031$ , that  $\bar{5}052$  is stronger than  $\bar{5}502$ ; this is particularly well shown in the Laue photographs. Such variation between planes approaching parallelism is of the utmost importance in determining atomic positions.

Considering the problem theoretically a preliminary attempt was made by taking account of the silicons only, a method similar to that adopted for  $\beta$  quartz. Symmetry conditions alone indicate that the silicon atoms can reside anywhere along the thin dotted lines of fig. 2 so long as the shift from the  $\beta$  position is the same for each; if they take up positions marked  $\bullet$  then it is convenient to express these new positions by fixing attention on the two triangular units  $abc$ ,  $a'b'c'$ , and to adopt as the variable the angle through which the triangle  $abc$  has rotated about an axis perpendicular to it through the point  $a$ ;  $a'b'c'$  will then turn through the same amount but in the opposite sense. Calculations showed that allowing for silicons only, a rotation of  $9^\circ$  was capable of explaining the observed results, as the few following planes indicate:—

Planes.	Intensity Observed Photographically.	Calculated Relative Amplitude.
$\bar{5}232$	Strong	2.0
$\bar{5}322$	Weak	0.4
$\bar{5}052$	Strong	2.7
$\bar{5}502$	Weak	0.6
$3031$	Weak	0.1
$3301$	Strong	3.0
$\bar{4}131$	Medium	1.6
$\bar{4}311$	Medium	1.1

By slightly increasing the rotation to about  $15^\circ$  the distance between the silicon atoms became sufficient to allow each oxygen atom to fit in line between two silicons, and its valency bonds to become diametrically opposite and therefore collinear. This possibility was tested for the planes  $mmn$ , making allowance for both silicon and oxygen atoms in proportion to their atomic weights. The following results show some agreement but fail as regards the  $mm\bar{o}3$  as well as the  $oon$ ; they are only included to emphasize the necessity of moving the oxygen atoms out of their  $\beta$  level.

Calculated.			
$m =$	1	2	3
$n = 3$	0.3	4.6	1.3
2	3.6	6.9	2.5
1	7.5	3.2	1.0
0	7.8	3.3	1.1
$\bar{1}$	11.3	4.4	5.2
$\bar{2}$	0.6	6.5	1.5
$\bar{3}$	0.3	4.6	1.3

It was easily proved that the tetrahedral arrangement of the oxygens around any silicon could not remain in the  $\alpha$  state, for this would entail a mere rotation of the tetrahedra, coupled with a possible translation perpendicular to the  $c$  axis. From symmetry conditions a rotation could not occur about the  $c$  axis because the dyad axes perpendicular to it remain unaltered. Further, rotation axes perpendicular to the  $c$  axis were not permissible, as they would shift two oxygen atoms previously in the same  $c$  plane to unequal extents above and below it. Several other suggestions were tried, but as all failed it became a somewhat lengthy problem of trial and error. Over two dozen complete sets of calculations were made, of these only the final data need be recorded.

In order to account for the basal plane intensities it was shown (these 'Proceedings,' vol. 107) that the oxygen planes should lie practically  $c/9$  above and below the silicon planes, which are themselves  $c/3$  apart. Thus it was decided to compound the two most hopeful results, viz., the known level of the oxygen atoms, and the small rotation about  $9^\circ$  of the triangles of the silicon atoms, whilst maintaining the same relation between any silicon and all its neighbouring oxygens. In this manner the oxygen atom has been partially fixed by assuming it to lie in two planes, one perpendicular to the  $c$  axis  $c/9$  above or below the silicon atom, the other perpendicular to the join of the two silicon atoms A, B, and passing through the mid-point M of this join. The first plane is parallel to the paper and passes through XY in fig. 3, whilst in fig. 4 it is

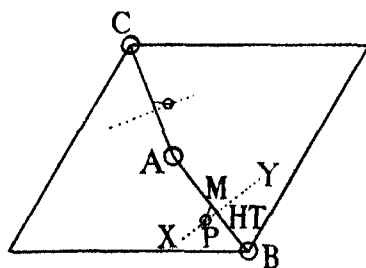


FIG. 3.

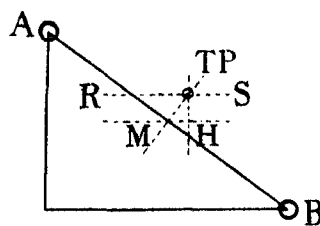


FIG. 4.

represented by its trace RS. The second plane contains MXPTY in fig. 3 and is represented by its trace MTP in fig. 4. The oxygen atom has now only linear freedom along the intersection XY of the two planes, and if situated at P the remaining parameter may be identified with MP, *i.e.*, the distance of the atom from the line joining the two silicon atoms with which it is in contact. Calculations were made for various values of the rotation parameter from  $4^\circ$  to  $16^\circ$  and for various values of MP. Finally a rotation of  $8^\circ$  associated with a

value of 0.44 A.U. for MP was found to give the best result. In figs. 3 and 4 the distances in A.U. corresponding to this arrangement are  $MT = 0.33$ ,  $PT = 0.29$ ,  $MH = 0.19$ ,  $MP = 0.44$ , distance AB between silicon atoms = 3.05, distance AP (= PB) between oxygen and silicon atoms = 1.59, APB between oxygen bonds =  $147^\circ$ . The distance between the oxygen atoms is no longer a unique quantity owing to the loss of tetrahedral symmetry; it is about either 2.72, 2.66, 2.50. The measure of agreement given by this structure is shown by the following planes, chiefly of the type  $nmn$ .

Observed.				Calculated.			
$m =$	1	2	3	$m =$	1	2	3
$n = 3$	0.0	6.5	2.0	$n = 3$	0.8	5.6	1.2
2	4.9	3.5	4.7 strong	2	4.5	2.0	3.95
1	10.0	4.1	0.0	1	7.0	2.8	0.06
0	7.3	5.0	2.5	0	5.0	4.8	1.6
-1	13.0	2.6	6.1	-1	11.5	1.8	6.2
-2	3.5	5.5	3.8 weak	-2	1.5	5.0	1.7
-3	3.8	4.6	1.1	-3	2.8	2.9	1.1
0003	3.0			0003	0.7		
0006	3.0			0006	0.6		
0009	2.5			0009	1.1 (reduces to 0.5 neglect-		
1120	5.7			1120	3.4 ing oxygen).		
2240	4.1			2240	2.9		

These results are shown in graphical form in figs. 5, 6 and 7. As was

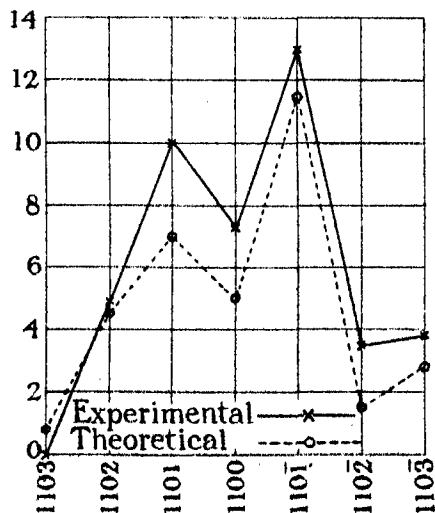


FIG. 5.\*

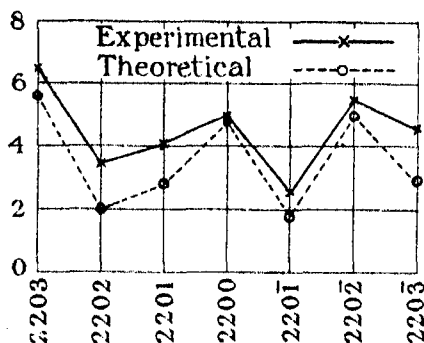


FIG. 6.\*

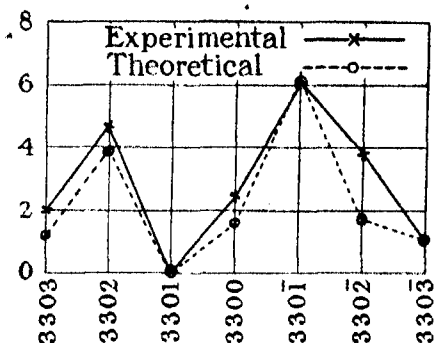


FIG. 7.\*

indicated by previous results, the structure is, over a wide range, probably dependent to a small extent on temperature, only changing at a rapidly increasing rate as  $575^\circ$  is approached.

Intensity calculations are not at present on a firm basis and it is impossible on any theory to obtain absolute agreement with experimental results. In this case the calculations recorded assume the reflecting powers of silicon and oxygen atoms proportional to their atomic weights, and allow for the falling-off with increasing glancing angle by using the factor  $1/\sin^2 \theta$ . Among the other assumptions tried were the proportionality of reflecting power to the number of electrons in the outer shells of the atoms in the ionised condition, and the use of the intensity factors calculated by Hartree, 'Phil. Mag.', July, 1925. These varied assumptions necessarily create a difference in the results but not so much as would appear at first sight, for their effects partially counteract, *e.g.*, if the reflecting power of the silicon is  $S$  and of the oxygen  $R$  then in the results given  $R/S = \frac{1}{4} \frac{8}{16}$  whilst on the other assumptions  $R/S = \frac{1}{10} \cdot F$ , where  $F$  is a structure factor. These results would be the same if  $F = 0.57$ , an average factor for intermediate spacings.

A large number of calculations was made, but in no case was a general agreement obtained as good as that recorded by using the assumptions which resulted in the solution of the  $\beta$  quartz structure.

Assuming now that the structure proposed is not far from reality then it is advisable to consider its merits. It satisfies symmetry conditions and gives a reasonable explanation of the intensity of reflections from a number of planes.

To enable some representation to be given of the change of structure from  $\beta$

\* A negative sign has been omitted in error over the second number throughout figs. 5, 6, and 7. These should read 1103, 1102, ..... 3303.



to  $\alpha$  quartz, figs. 8-13,\* the atomic diameters of silicon and oxygen have been assumed to be 1.87 and 1.30 A.U. respectively. The changes show that the tetrahedra of oxygens have been twisted and slightly distorted, they also show the distinction which has arisen between the R and z planes and the possibility of a rhombohedral cleavage. The tunnels in the direction of the trigonal and digonal axes remain about the same dimensions, and should be large enough for some stranger atoms to navigate. This is of importance in view of the researches of Joffé on the "Electrical Conductivity of Crystals" ('Ann. d. Phys.,' 1923).

In order to illustrate the alteration in the intensity of reflection at a particular temperature caused by rapidly cooling a specimen through its transition point, a few Laue photographs of such specimens were taken. These together with some spectrometer measurements showed that the hexagonal symmetry which had apparently been retained was due not to the  $\beta$  structure but to a twinning of the  $\alpha$  in such a way as to simulate a hexagonal symmetry about the c axis. In one case the crystal remained transparent but showed signs of fine cracks, whilst in another the cooling was so rapid that the crystal became completely opaque and of a powdery nature: both gave equally good Laue photographs so that although the crystal had been completely "smashed," yet the relative movements were not sufficient to mar to the smallest extent the X-ray crystal-line reflections. It is apparent therefore that the quartz transition is a very sharp one, and that slower cooling only enables the resulting structure to be less twinned.

In connection with practical mining problems in which quartz material has to be crushed, difficulty arises owing to its hardness, and an attempt to break down the material is made by cooling it rapidly from a high temperature. The previous results indicate that the efficacy of this method is associated with a very rapid rate of cooling, and, secondly, with only a narrow range of temperature. Rapid cooling over a very small range, including the transition temperature, is all that is required, and probably one or two repetitions over this range would be more effective than one cooling over a larger range.

During the transition two influences appear to exert separate actions in controlling the structure, one being associated with the structure of the silicon atom exhibited in its tetrahedral bonding, the other with thermal agitation. As the result of greater freedom, due to an increase of the latter, above 575°, the tetrahedral character is the more effective, but below this temperature

\* The apparent dissymmetry on the right of figs. 12 and 13 is merely a consequence of the shape of the volume selected for projection; the diagrams are elevations of the hexagonal prisms, the basal projections of which can be seen in figs. 8 and 9.

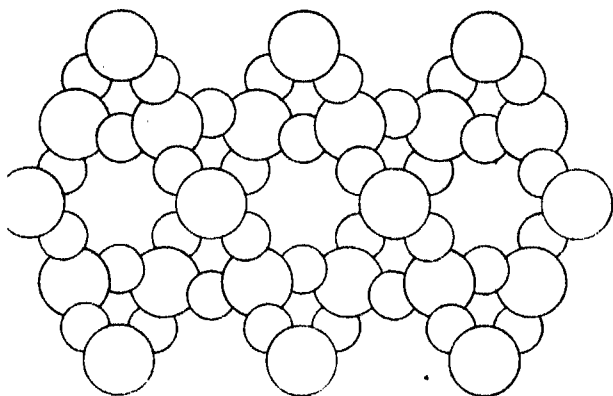


FIG. 8.— $\beta$  Quartz along  $c$  axis.

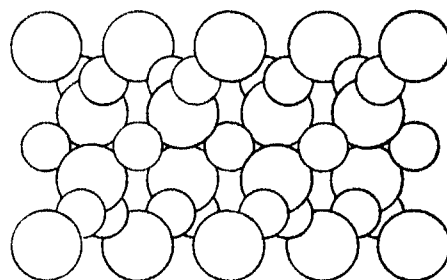


FIG. 10.— $\beta$  Quartz perpendicular to an  $a$  axis.

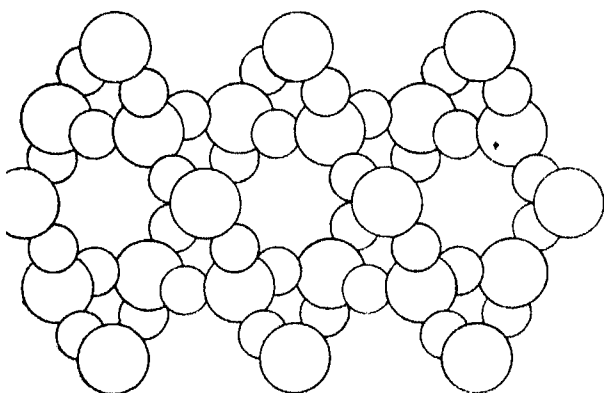


FIG. 9.— $\alpha$  Quartz along  $c$  axis.

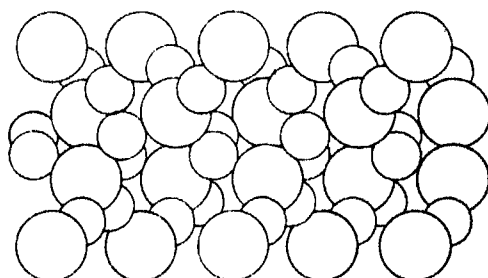


FIG. 11.— $\alpha$  Quartz perpendicular to an  $a$  axis.

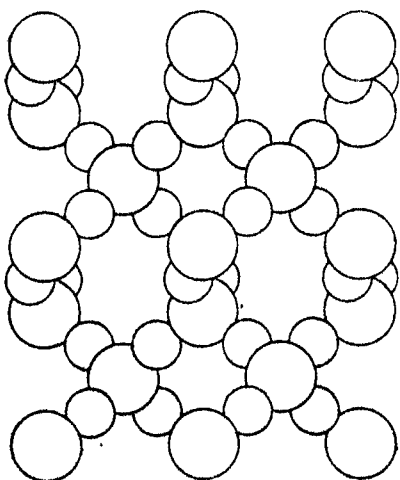


FIG. 12.— $\beta$  Quartz parallel to an  $a$  axis.

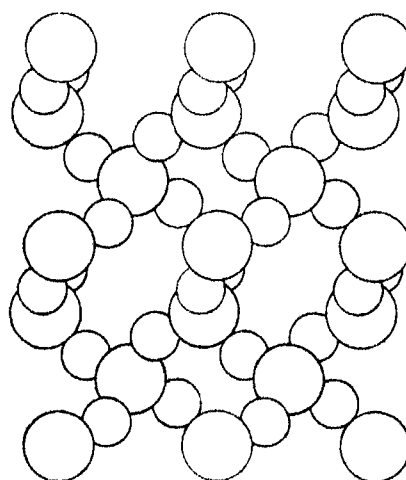


FIG. 13.— $\alpha$  Quartz parallel to an  $a$  axis.

the thermal contraction introduces constraints sufficient to distort the structure and lower its symmetry without the apparent conservation of any particular principle. Perrier and Mandrot demonstrated the loss of elasticity at the transition point, but the value at the exact temperature might be lower than that which they obtained, for with so sharp a variation in the curve the lower limit would be difficult to record. This loss of elasticity is probably associated with a very sharp balance between opposing forces.

Lastly, it is interesting to see what explanation of the pyro- and piezo-electric effects can be offered by the suggested structure. It has already been shown that a trigonal group of three silicons and three accompanying oxygen atoms may be chosen in plan as a unit of pattern. Two of these units point in exactly opposite directions in  $\beta$  quartz, fig. 14A (employing merely skeleton triangles), and only nearly so in  $\alpha$  quartz, fig. 14B. Each silicon at an apex of the triangles may be regarded as the seat of a positive charge  $4e$ , and each

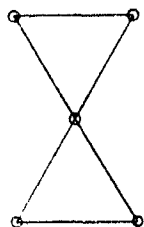


FIG. 14A.

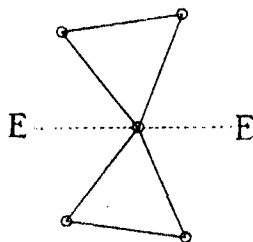


FIG. 14B.

oxygen near the mid-point of a side as that of a negative charge  $-2e$ . As each silicon touches four oxygens, and each oxygen two silicons, the complete structure can be represented by electric doublets, one corresponding to each valency and equal to the product of the electronic charge and the distance between the centres of the silicon and oxygen atoms. This is, of course, a big assumption, neglecting the finite size of the atom and the effect of any atom or electron on its neighbours. It is inaccurate, but may suffice for elementary calculations where other factors are somewhat uncertain and only a first approximation can be expected. Fig. 14A is a symmetrical balanced structure on any hypothesis, but  $\alpha$  quartz, fig. 14B, is unsymmetrical and has certain electric axes EE in which directions resultant electrical forces may exist. Each separate triangular group will exhibit a trigonal field in its neighbourhood, but at greater distances will approximate to a balanced system. The resultant of a large number of such groups in the structure will be a field the trigonal nature of which will extend to greater distances. Any change which causes

the triangles  $abc$ ,  $ab'c'$  of fig. 2 to rotate relatively to one another will alter the fields acting along all the electric axes.

The external field of all the internal doublets is masked by the accumulation of surface charges. due to ionisation in the air, etc., sufficient exactly to counter-balance it. Normally, therefore, the quartz crystal appears externally neutral, and it is only when the internal electric forces change that they become externally manifest, until once again there is an adjustment of the neutralising surface charges. The internal forces have changed, therefore, when the presence of pyro or piezo-electricity is noted.

In the case of quartz, whereas pyro-electric charges accompany temperature changes, a hydrostatic pressure has no electrical effect. It might appear that, as both cause expansion or contraction, they should excite the same electric charges, but experimentally this is not so. The distinction lies, probably, in the fact that temperature changes affect chiefly the kinetic energy of thermal agitation of the atoms, whilst a hydrostatic pressure should alter mainly their potential energy. As previously mentioned, a variation of temperature is probably accompanied by a small change of structure, a relative rotation of the triangles  $abc$ ,  $ab'c'$  of fig. 2, and a corresponding movement of the oxygen atoms: such a change would result in the alteration of the internal fields and account for the observed generation of pyro-electricity. This would occur accompanied by the usual linear changes but without distortion, so that the crystal would remain uniaxial.

It is convenient to resolve a hydrostatic pressure on a hexagonal quartz crystal into four separate pressures, one parallel to the optic axis and three perpendicular, one parallel to each electric axis, and to consider the effect of each separately. Under these forces the crystal will remain uniaxial. According to experimental piezo-electric laws, the force along the optic axis does not generate any charges, nor do the latter three along the axes acting together, although separately each would produce piezo-electric charges. These charges would result from the distortion of the crystal and a temporary loss of its uniaxial symmetry. If for the moment ordinary piezo-electric charges are assumed to be partly dependent on the relative rotation of the silicon triangles, then it can be shown that the rotations due to the forces along all the electric axes are in the same sense, and that when acting together the rotations would be added arithmetically. This would mean that charges would be developed by a hydrostatic pressure in the same manner as by heat. It appears necessary to attribute pyro-electric charges to rotation and not to distortion, and hence as a hydrostatic pressure is unaccompanied by charges,

piezo-electricity must be governed by distortion alone. The two effects would be due, therefore, to different causes; pyro-electricity to change of structure towards or away from hexagonal symmetry, piezo-electricity to mechanical distortion of structure involving loss of uniaxial nature. Both arise from the redistribution of electric charges in the crystal and in each case the external effects are only a measure of the change of small quantities which are themselves differences of nearly-balanced systems of electrical doublets. Any calculations made concerning them must of necessity only be undertaken to see if even the order of magnitude of the quantity is reasonable.

Approximate calculations have been made for the case of a rectangular quartz slab, cut with its three main axes respectively parallel to the optic axis, and perpendicular or parallel to one electric axis. The simplest case arises when the crystal is subjected to a pressure parallel to the electric axis. Two methods of procedure are possible, either the moment parallel to EE of each valency in the triangle may be calculated and a summation made for a given volume, or, alternatively, the relative shift of the centres of gravity of the silicon and oxygen triangular units may be calculated, and its component parallel to EE multiplied by the charge density of the substance. Both methods necessarily lead to the same end, and being of about equal simplicity there is little to choose between them.

Adopting the second method, attention was focussed primarily on the silicon atoms, the distortion of whose structure was deduced from the elasticity coefficients given by Voigt ('Ann. d. Phys.,' vol. 31, 1887). The component parallel to EE of the displacement of the centre of gravity of the silicon triangle proves to be very small, about  $0.3 \cdot 10^{-21}$  cm., for a pressure of one dyne per square centimetre. A corresponding calculation for the oxygen atoms is beset with considerable uncertainty; even in the undistorted structure the positions of these atoms could only be estimated from intensity observations, and without further experiments the displacements resulting from distortion are indeterminate. On the assumptions that the atomic diameters remain unaltered, and that the plane containing any two neighbouring silicons and the intervening oxygen maintains a constant inclination to the *c* axis, the component parallel to EE of the shift of the centre of gravity of the oxygen triangle is  $6.3 \cdot 10^{-21}$  cm. This results in a relative average displacement of positive and negative charges of about  $6 \cdot 10^{-21}$  cm.

For comparison the separation can be calculated from the experimental value  $6.8 \cdot 10^{-8}$  of the piezo-electric constant. The density of the electric charge in the crystal is  $4ne$ , where *n* is the number of silicon atoms per c.c., it is

$5.06 \cdot 10^{13}$ . Thus, the displacement should be  $1.34 \cdot 10^{-21}$  cm., which means that the calculated piezo-electric constant is just over four times too large. The choice of other assumptions governing the movements of the oxygen atoms might permit this lack of agreement to be eliminated, but a more accurate result than the above could hardly be expected on elementary principles, nor in fact would it be of any greater value than suggesting the order of magnitude of the piezo-electric constant.

In conclusion, I desire to express my best thanks to Sir William Bragg for his unfailing interest and useful suggestions, and my indebtedness to the Department of Scientific and Industrial Research for financial aid. Thanks are due also to Prof. Gordon for his ready help in preparing specimens, to Miss Yardley to whom some of the spectrometer data are due, and to members of the research staff whose help expedited this work.

#### *Summary.*

Investigations on quartz have shown that the symmetry and X-ray data enable the structure to be only partially defined. A complete determination involves more parameters than can be evaluated by this means, and for the solution of the remaining four unknown variables, intensity measurements and general physical properties of the material have to be studied.

Observations of the intensities of reflection from a number of planes were made by oscillation, rotation, Laue photographs, and on the ionisation spectrometer. By their aid it was proved that the oxygen atoms do not lie either in the same basal planes as the silicons or half-way between, but rather occupy positions  $c/9$  above and below them.

The variation in the values of the physical properties is in favour of only a small structural change accompanying the transition from  $\beta$  to  $\alpha$  quartz, but still the tetrahedral character of the former structure must be lost. The structure proposed assumes the crystal to be non-molecular and the oxygens to occupy basal planes as noted above. Evidence is advanced for a movement of the silicon atoms of about 0.3 A.U. from their  $\beta$ -positions, and intensities were calculated for various values of the remaining two parameters.

The possible distinction between the causes of pyro- and piezo-electricity are discussed, and a calculation shows that, on the assumption made, the coefficient deduced for the latter agrees in order of magnitude with the accepted value.

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*The Determination of the Vapour Tensions of Mercury, Cadmium and Zinc by a Modified Manometric Method.*

By C. H. M. JENKINS, B.Sc., A.R.S.M., of the National Physical Laboratory.

(Communicated by Dr. W. Rosenhain, F.R.S.—Received November 11, 1925.)

This research, conducted in the Metallurgical Department of the National Physical Laboratory, arose out of investigations on alloys of cadmium and of zinc, and had as its object the development of a method for determining the vapour pressure of such alloys.

In this method the substance under examination is used as the liquid in the manometer, which is employed to indicate a balance between the vapour tension of the substance with an externally applied pressure of nitrogen.

The measurement is made by statical means, the vapour being in contact with a free surface of the liquid. The substance is therefore not superheated at the time of measurement.

The study of the vapour tensions of metals, at other than very low pressures, has usually been undertaken by methods which have required actual ebullition. These suffer from two disadvantages: firstly, the difficulty of producing actual ebullition at moderately low pressures, when a condition of fuming tends to occur; and secondly, the liability of superheating the vapour. In the case of liquids boiling at moderately low temperatures, statical methods have been used so that the vapour has not been superheated.

The method depending on the observation of ebullition (1) is applicable to all ranges of temperature, probably up to 2500° C. In a more recent method (2) the vapour tension of lead was measured by suspending a thermocouple in the vapour above the boiling liquid. A constant temperature zone was found to exist above this surface; the temperature of this probably represents the condensation point of the liquid. A further method (3) not involving ebullition employed a fused silica Bourdon gauge: by balancing the internal pressure of this with an externally applied one, the results have reached a high degree of precision.

*Description of Apparatus.*

The manometer consists of a tube approximately  $\frac{3}{8}$  inch internal diameter and 18 inches in length, bent into a 60° V in the manner shown in fig. 2. In the closed end of the V-tube a sealed thermocouple sheath is inserted, projecting into this tube for approximately  $\frac{1}{4}$  inch.

For the determinations on mercury the manometer was made of glass ; but for temperatures above 500° C., such as were required for cadmium and zinc, the apparatus was constructed of fused silica. Owing to the possible absorption of metal by small cavities in the walls of the silica, a new apparatus was used for each metal.

Into the straight portion of the manometer tube three or more pieces, as shown in figs. 1 and 2, are inserted. The tube is thus converted into a fractionating

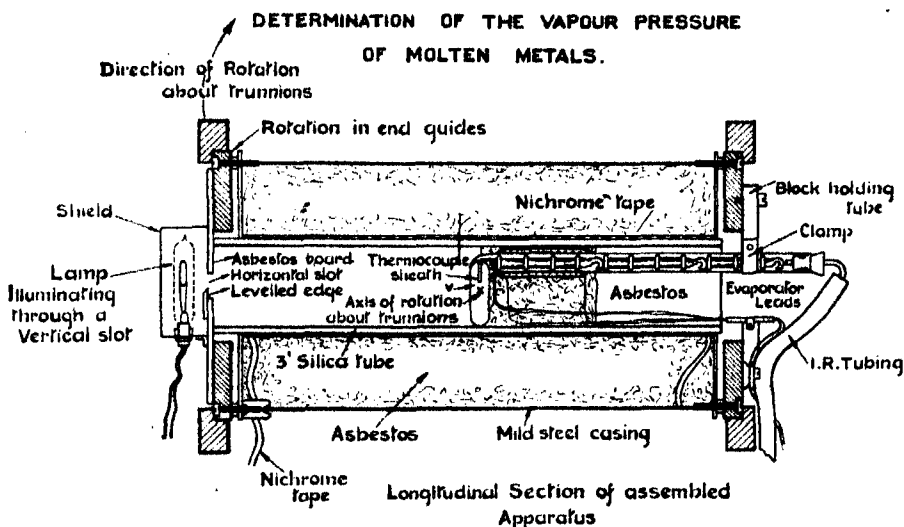


FIG. 1.—Longitudinal section through apparatus erected in furnace.

column of a type similar to a reflux condenser. A portion of the straight tube near the V bend is specially heated by a current in a nichrome winding, and is thus converted into an evaporator. The remainder of the tube, cooled as the outside of the furnace is approached, constitutes a condenser for the metallic vapour from which the liquid gravitates back to the evaporator. A steady heating current is maintained through the winding on the evaporator, supplying to the tube 15 watts in the case of the mercury determinations, and as much as 50 watts in the case of zinc. The stream of metallic vapour proceeding from the evaporator to the condenser counteracts the diffusion of the nitrogen, which is used to transmit the pressure to the external mercury barometer.

The manometer, containing the liquid under examination, is heated to the required experimental temperatures by means of a silica-tube furnace, 3 inches in internal diameter, having a nichrome-wire winding capable of maintaining the apparatus at temperatures up to 1100° C. A longitudinal section of the apparatus is shown in fig. 1.



The furnace is mounted in a frame which permits of its rotation about two axes at right angles—circumferentially in the end plates and in a vertical plane



FIG. 2.—Photograph of V-tube, showing pyrometer sheath and insert.

about the trunnions. These respective motions rotate the manometer in its own plane and in a plane at right angles. This allows the V apparatus to be brought into the three essential positions shown in fig. 3 :—

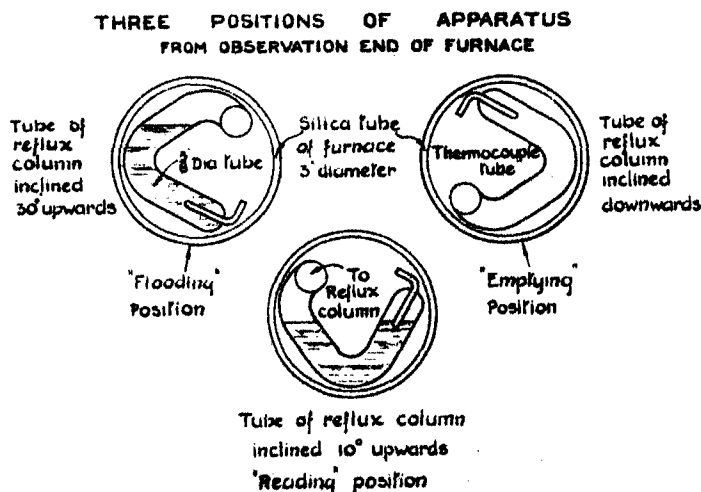


FIG. 2.

(1) The *flooding position*, in which the closed end of the V is brought to the bottom of the furnace. The V portion is inclined  $30^\circ$  by rotation in the trunnions, so that the end of the tube outside the furnace points upwards.

(2) The *reading position* is similar to the normal position of the letter V; the projecting end of the tube is inclined  $10^\circ$  upwards.

(3) The *emptying position* is obtained by rotating the V portion so that the closed end is at the top; the projecting end of the tube is then slowly inclined  $30^\circ$  downwards.

The temperature of the metal contained in the manometer is determined by means of a calibrated platinum-platinum-rhodium thermocouple, which remains just immersed in the liquid when a determination is being made.

The surfaces of the liquid in the manometer are most readily seen at temperatures below  $650^\circ\text{C}$ . by reflected light obtained by an electric bulb situated outside the furnace, as shown in fig. 1, but above  $650^\circ\text{C}$ . no external illumination was found to be necessary. By suitable variation in the nitrogen pressure the liquid in the V-tube can be moved slowly both up and down, thus ensuring that both surfaces in the manometer are free from any condensed liquid. The liquid surfaces are then clearly seen. The level of the surfaces in the manometer, which is situated in the centre of the furnace, is obtained by means of a levelled knife-edge.

The pressure on the apparatus is controlled by means of nitrogen supplied under pressure from a cylinder and by a vacuum pump, as shown in fig. 4.

#### DIAGRAM OF NITROGEN CONTROL

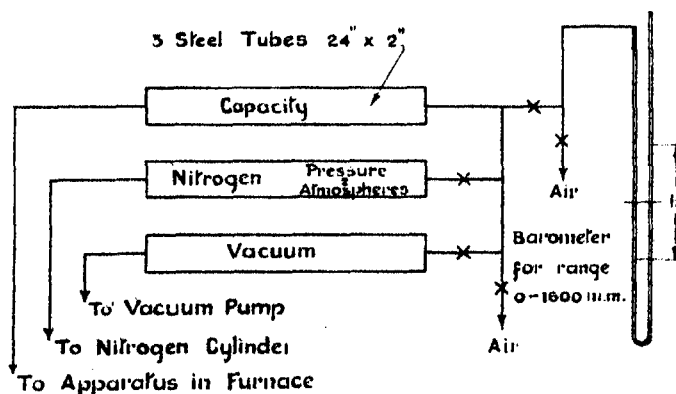


FIG. 4—Diagram of nitrogen control, showing connections for alteration of the gas pressure.

The three tubes, seen in this figure, were added to increase the capacity of the system and facilitate pressure adjustment by the controlling taps.

Entrapped gases, which cause considerable difficulty in the use of a closed manometer, are removed, and the manometer filled by the rotation of the V-tube into the "flooding" position. Before making determinations the liquid is boiled at a vapour tension of at least 100 mm. This can be carried out by reducing the pressure on the liquid in the flooded manometer below the ebullition point. This operation ensures the complete removal from the walls of the tube of entangled gas bubbles other than those of the vapour of the liquid under determination. After the boiling operation the pressure is increased above the ebullition point before returning the manometer to the reading position.

Pressure in excess of the vapour tension is maintained on the apparatus except during a determination or the deliberate boiling of the metal. This excess pressure, if kept about 200 mm., is sufficient to prevent loss of metal by evaporation, so that the apparatus can be left for many hours, with sufficient liquid remaining in the manometer to permit of readings being taken without tilting it into the "flooding" position. It is found possible to take many readings without allowing nitrogen to enter the closed end of the V.

#### *Determination of the Vapour Tension.*

The liquid is brought to occupy the closed end of the manometer by first flooding the V and then bringing the tube into the "reading" position under an excess pressure. Readings of the vapour tension are then taken by adjusting the pressure at steadily maintained temperatures. The pressure is gradually reduced until the two liquid surfaces in the V apparatus are level. At this moment the pressure and temperature are noted by reading the barometer and the potentiometer. The level so obtained should remain constant for a few minutes without noticeable alteration.

On the completion of each set of determinations the furnace is cooled from near the maximum temperature by switching off the heating current. During the cooling, determinations of the vapour tension and temperature are taken as rapidly as possible. The entire readings for one metal, given in Table III, are taken over a time interval of from 15 to 25 minutes. These results are found to be in close agreement, generally within  $1^{\circ}\text{C.}$ , of the results obtained under steady furnace conditions, indicating the absence of serious thermal gradients in the apparatus.

The experimental results are given in Table I for the three metals—mercury, cadmium and zinc—and are shown plotted in fig. 5. Mean values deduced from a large-scale plotting are given in Table II. This shows the boiling point

(760 mm.) of the three metals—mercury, cadmium and zinc—to be 357° C., 767° C., and 906° C., respectively.

The determinations have been carried out upon mercury, as it was considered that this would afford a check on the accuracy of the method in view of the values already known for this metal.

From the methods employed, it is thought that the accuracy of the pressure

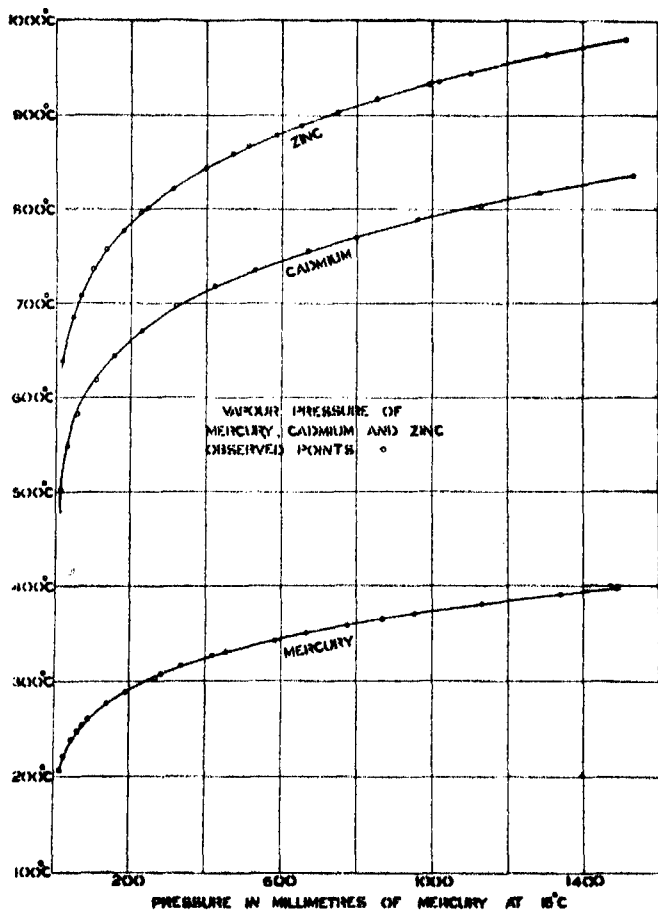


FIG. 5.

readings in the present investigation is approximately 2 mm., and that of the temperature about 1° C. at 600° C.; therefore, at pressures over 100 mm. for mercury, 160 mm. for cadmium and 180 mm. for zinc, the pressure measurement is probably more accurate than the temperature. This point will be appreciated when it is considered that the alteration in the pressure at the boiling point (760 mm.) in the case of mercury is approximately 14 mm. of mercury per

1° C., cadmium 8 mm. and zinc 7 mm. It thus appears that by this method the boiling point can be determined as closely as the normal reading of a thermocouple will permit.

#### *Conclusions.*

Although in the present paper the apparatus has been adapted for the determination of the vapour tension of these three metals, the existing form, whether mounted in a furnace or heated in a jacket of a transparent liquid, is also suitable for most liquids.

By taking suitable precautions to guard against alterations in composition, or by checking the composition, the apparatus affords a means of determining the total vapour tensions exerted by molten alloys.

The comparatively large alterations in pressure produced by small alterations in temperature provide a basis for constructing a vapour-pressure thermometer which is capable of measurement of small variations in temperature at high temperatures. This permits of accurate comparative measurements of temperature to be carried out in terms of vapour tensions of high boiling-point liquids, which are comparatively easily reproducible.

The author wishes to express his thanks to Dr. W. Rosenhain, F.R.S., for his interest and encouragement during the progress of the research.

Table I.—Observed Values determined on the Apparatus maintained for 10 minutes at a Steady Temperature prior to the Reading.

Mercury.		Cadmium.		Zinc.	
° C.	Mm.	° C.	Mm.	° C.	Mm.
206	17	503	15	629·5	19
220·5	28·5	549	32	686	48
238	48·5	583	60	709	68
247·5	62	619	110	737	101
253	76	645	159·5	758	135
259·5	91	671	231	778·5	183
276·5	139	698	322	797	229
288·5	188·5	718·5	424	802	244
303·5	267	736	529	822	313
308·5	284	756	672	844·5	401
316·5	335	771	799	860	472
327	417	789	961·5	868	512
331	455	804	1131	880	589
342	582	818	1286	889·5	653
350	664	836	1535	904	749
358	773	—	—	918·5	853
364·5	867	—	—	934·5	992
370·5	952	—	—	937·5	1020
380·5	1131	—	—	946	1104
391	1342	—	—	965·5	1305
397·5	1490	—	—	982·5	1517

Table II.—Mean Values obtained from the Plotted Data.

Mercury.		Cadmium.		Zinc.	
° C.	Mm.	° C.	Mm.	° C.	Mm.
200	14	500	14	625	16
225	30	525	23	650	28
250	68	550	38	675	42
275	137	575	56	700	60
300	245	600	82	725	85
325	407	625	119	750	122
330	450	650	170	775	172
340	540	675	240	800	240
350	667	700	334	825	326
357	760	725	463	850	427
360	805	750	628	875	557
375	1045	767	760	900	717
397.5	1490	775	829	906	760
		800	1078	925	908
		825	1383	950	1145
—	—	836	1535	975	1426
—	—	—	—	982	1517

Table III.—Readings taken while the Furnace cooled rapidly.

Mercury.		Cadmium.		Zinc.	
° C.	Mm.	° C.	Mm.	° C.	Mm.
379	1114	809	1176	954.5	1299
354.5	725	794	1025	951	1176
341.5	563	782	898	923.5	914
325.5	407	761	703	907.5	778
312	312	723	450	889.5	649
301.5	249	712	389	875.5	559
292	200	697	317	857	460
282.5	164	689	289	836.5	369
259.5	91	663	204	817	297
		630	130	791.5	216
—	—	—	—	767.5	159
—	—	—	—	727	92

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*Critical Potentials of Hydrogen in the Presence of Catalytic Nickel and Copper.\**

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(Communicated by Dr. E. F. Armstrong, F.R.S.—Received December 8, 1925.)

A recent paper by A. W. Gauger† opens the possibility of an interesting and novel method for gaining information on the mechanism of hydrogenation catalysis by nickel and other metals. Gauger bombarded with electrons a target of catalytic nickel in the presence of a low pressure of hydrogen, and observed the critical electron velocities at which the occurrence of characteristic radiation could be detected by the photo-electric current which it produced by falling on a collecting plate connected to an electrometer.

Gauger reported a number of critical potentials, several of which he associated with the first members of the Lyman series and the ionisation of atomic hydrogen respectively. The results were interpreted as indicating the presence of atomic hydrogen in the system comprising hydrogen and a nickel catalyst.

A closer examination of this very suggestive work seems to reveal certain defects of method which render rather equivocal any conclusions drawn from the results obtained. The following criticisms are suggested :—

- (1) An examination of the specimen curve in Gauger's paper (which was printed upside down relative to the co-ordinates, owing to a printer's error) shows that all except two of the breaks shown are "negative" breaks ; that is to say, the radiation increases less rapidly with voltage above the critical potential than below it. Breaks of this type are comparatively rare,‡ and have never been reported by any other investigator of the critical potentials of molecular or atomic hydrogen. The as yet unpublished work of C. H. Thomas on soft X-rays from nickel also fails to show a negative break associated with any of the numerous critical potentials observed. This unusual form of the curve suggests that perhaps some of the observed breaks are fictitious.

\* Contribution from the Laboratories of Physics and Physical Chemistry, Princeton University, Princeton, N.J., U.S.A.

† 'J. Am. Chem. Soc.,' vol. 46, p. 674 (1924).

‡ Kurth, 'Phys. Rev.,' vol. 18, p. 468 (1921).

- (2) The aggregate correction for initial electron velocity and contact potentials seems to have been applied wrongly. As far as one can determine from the paper, the correction should have been added and not subtracted. This would increase all the observed critical potentials by 0.4 volt.
- (3) The magnitude of this aggregate correction seems to be incorrect for two reasons: first, because the method of application assumes that the relative sensitivities of the apparatus for detecting radiation and primary electrons are the same\*; secondly, because the overall contact potential corrected for is that between the filament (tungsten) and the plate (platinum) connected to the electrometer, whereas the contact potential involved in the main experiments is that between the filament and the target of catalytic nickel.

Summarising the criticism relative to the correction for initial velocities and contact potentials, it is submitted that the critical potentials reported by Gauger are subject to a correction of

$$+ 0.4 - x \mp y \text{ volts,}$$

where  $x$  depends on the difference in sensitivity of the apparatus for detecting radiation and for detecting primary electrons, and  $y$  is the contact potential between platinum and the catalytic nickel target employed.

- (4) A final uncertainty arises as to the origin of the radiation measured. It is conceivable that hydrogen gas in the absence of the catalytic metal might have given breaks characteristic of atomic hydrogen, owing to thermal dissociation by the hot tungsten filament. And even if this possibility is excluded, there are still three alternative sources of the radiation—namely, the mass of residual hydrogen gas, the hydrogen at the catalyst surface, and, finally, the catalytic metal itself. Blank experiments with no gas present negatived the last of these alternatives, but none of the experiments performed served to determine whether the effects observed originated in the body of the gas or at the catalyst surface.

The present work aimed at a repetition and extension of Gauger's work, modifying the method in such a way as to eliminate the features which make his results of an equivocal character. In particular, the correction for initial velocity and contact potentials has been applied in such a way as to put the

\* Smyth, 'Phys. Rev.', vol. 14, p. 409 (1919).



absolute values of the critical potentials on a surer basis. Furthermore, by comparison with results obtained when the preponderating effect was due to a body of plain molecular hydrogen, evidence was afforded that the effects measured were associated with the hydrogen at the catalyst surface. The work has been extended to compare the effect of catalytic nickel with that of plain nickel and also that of catalytic copper.

#### *Materials and Apparatus.*

Catalytic nickel was prepared by the reduction of the oxide by hydrogen at 370° C. The oxide was prepared by the ignition of a thin film of chloride-free nickel nitrate solution spread over a thin rectangular plate of massive nickel.

Catalytic copper was prepared in an exactly similar manner except that the reduction was carried out at 200° C. In both these cases and in the case of the plain nickel target, the metal was heated to redness *in vacuo* by an induction furnace before the application of the catalytic layer.

The apparatus is illustrated in fig. 1. The drawing is roughly to scale, the diameter of the central bulb being 9 cm. and the distance between target and collecting disc being about 2.5 cm. The electrical connections are essentially the same as those employed by Gauger, except for the modification necessary to admit of the measurement of ionisation currents as well as radiation effects. Electrons from a notched platinum strip coated with barium and strontium oxides are accelerated towards the target of catalytic metal, which rests on a water-cooled copper butt-end. The radiation produced falls on a platinum disc connected with a Compton electrometer (whose sensitivity remained very steadily at about 2,300 mm. per volt). Between the target and the collecting disc are placed three platinum gauzes whose voltages (illustrated on the diagram) are arranged to prevent any ions or electrons from reaching the collecting disc. Thus, with the voltage of the middle gauze at 52 volts, the electrometer readings measure the photo-electric current due to the radiation from the target and from the gas between filament and target. By means of a switch, the voltage of the middle gauze could be changed to 8 volts, under which circumstances positive ions are accelerated towards the collecting disc, so that the combined effects of ionisation and radiation are observed in the electrometer current.

The targets are mounted along two parallel thin nickel wires connected at their ends to two cylinders of soft iron. By the use of an electromagnet it is possible to bring any one of the targets in front of the electron source and in contact with the water-cooled butt-end.

The leads to the filament are introduced through a tube which enters the central bulb perpendicular to the plane of the paper. All ground-glass joints are made tight with de Khotinsky cement, which is disposed so as to reduce the vapour pressure of the cement within the apparatus to a minimum.

The experimental tube is connected through two liquid air traps to a hydrogen generator (in which hydrogen was generated by the electrolysis of baryta solution), a McLeod gauge and a mercury diffusion pump. Before use the

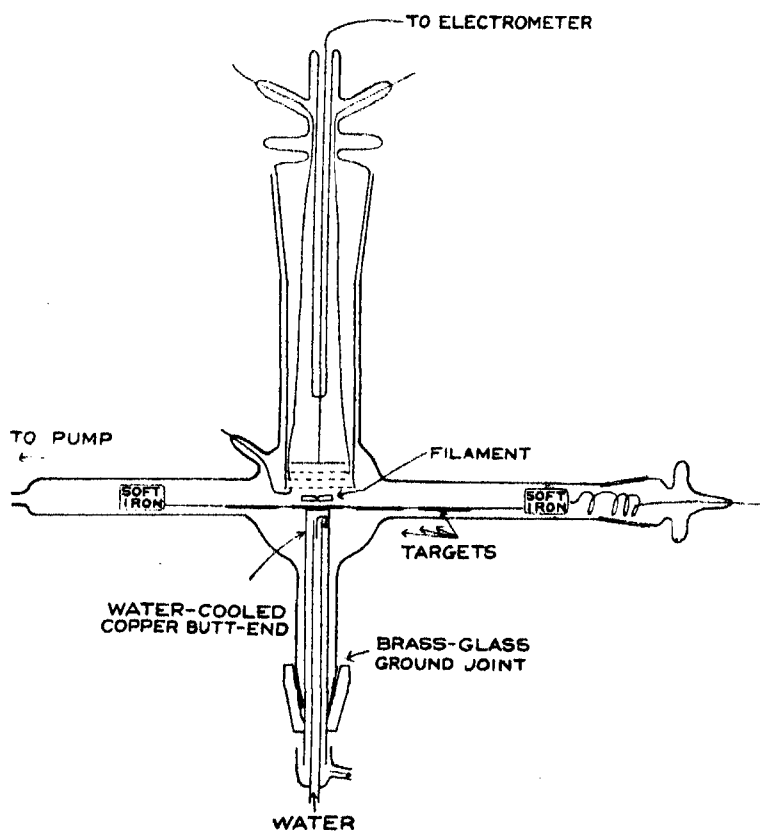


FIG. 1.—APPARATUS.

Voltage Scheme ; Collecting Plate .....	0 volts.
Grid (1) .....	6 volts.
Grid (2) .....	8 or 52 volts.
Grid (3) .....	9 volts.
Filament .....	16 volts.
Target .....	$18 + V_A$ .

tube was baked out *in vacuo* for about ten hours at  $370^\circ$ . Higher temperatures would have de-activated the catalysts.

The differences between this experimental tube and that employed by Gauger consist essentially in the use of an oxide-coated filament with correspondingly smaller chance of thermal dissociation in the device, which permits of the use of several targets without opening the tube, and in a general arrangement by which the collecting disc subtends a considerably greater angle at the target with a correspondingly greater sensitivity for detecting radiation and by which a closer spacing between filament and target accentuates the effects from the catalyst surface relative to those originating in the body of the gas.

#### *Experimental Procedure.*

The filament current was switched on, about 6 amperes being sufficient to raise the filament to a dull red heat which gave the desired thermionic emission. Hydrogen was admitted to a pressure of about 10 mm. of mercury and allowed to remain in contact with the target for five minutes. Pumping was then started, and as soon as the pressure had fallen to  $2 \times 10^{-4}$  mm., the first readings were taken.

As the accelerating voltage was raised in steps of 0.25 volt, observations were made of the electrometer current and the thermionic current between filament and target (measured on a micro-ammeter) corresponding to each value of the accelerating voltage. The experimental curves were obtained by plotting accelerating voltage ( $V_A$ ) as abscissa, and the quotient of electrometer current divided by thermionic current as ordinate. At the lower voltages the electrometer current was measured by "rate of deflection"; at the higher voltages, shunts were introduced, and the "constant deflection" method employed.

#### *Results.*

*Radiation Effects with Plain and Catalytic Nickel.*—The first experiments consisted in a repetition of Gauger's work, employing a tungsten filament and measuring the photo-electric current due to radiation only. Determinations were made with both plain nickel and catalytic nickel as targets. Many curves were obtained, of which curves (1) and (2) in fig. 2 are typical examples. Curve (1) is for catalytic nickel and curve (2) is for plain nickel.\* Except for minor irregularities, which the study of a large number of curves showed to

\* In these curves and in those that follow, the ordinates are of arbitrary magnitude; furthermore, in order to get curves for comparison in juxtaposition on the same diagram, the horizontal zero axis has been shifted up and down for the various curves on the same diagram. All voltages are uncorrected observed voltages.

be absolutely random in their occurrence, it is clear that the curves are smooth ones without any readily located discontinuities, and also that catalytic and plain nickel show no perceptible difference from one another.

It was concluded that no results bearing any simple interpretation would

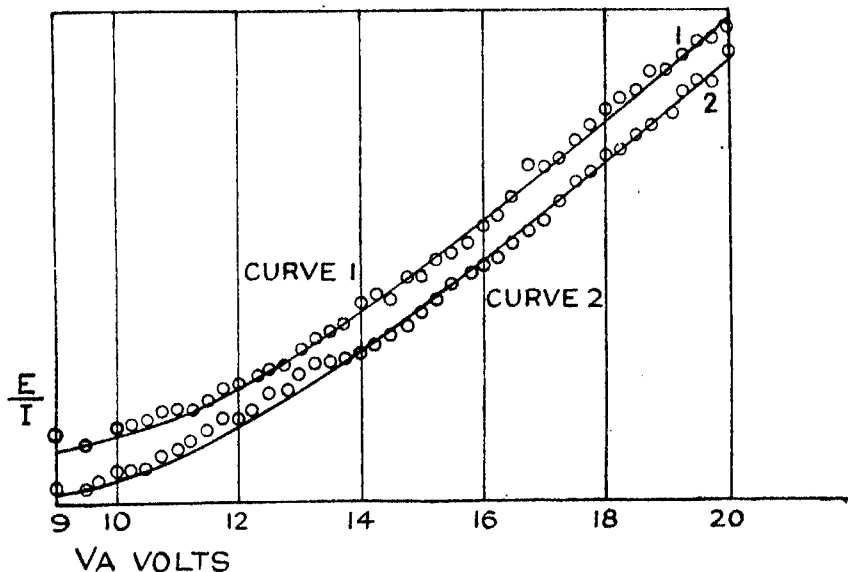


FIG. 2.—Radiation only.—Curve (1): Catalytic nickel.  
Curve (2): Plain nickel.

be obtained by this method. The decision was therefore made to measure ionisation currents instead of radiation effects alone in the subsequent experiments. The study of ionisation rather than radiation has several advantages :—

- (1) The currents to be measured are considerably greater.
- (2) The results are more readily interpretable. While the radiation potentials of both atom and molecule are numerous, and not entirely of uncontroversial origin, the ionisation potentials of the atom at 13.4 volts, and of the molecule at 16 volts are strongly marked and unambiguous.
- (3) By the simple device of carrying out several runs at a pressure of  $10^{-2}$  mm. of hydrogen, it is possible to make an unequivocal determination of the aggregate correction for initial electron velocity and contact potentials. Under such conditions the effects observed are due almost exclusively to molecular hydrogen, so that the location of the single strong break in the resultant curves determines the value of the observed voltage corresponding to a true electron velocity of 16 volts.

Arguing from these considerations, all subsequent experiments were carried out by measuring ionisation currents and employing an oxide-coated filament.\*

*Ionisation Measurements with Plain and Catalytic Nickel.*—Measurements were carried out with plain and catalytic nickel at  $10^{-4}$  mm., and at  $10^{-2}$  mm. pressure of hydrogen. Specimen curves are shown in fig. 3. (Curve (3) shows the result with a pressure of  $10^{-2}$  mm.

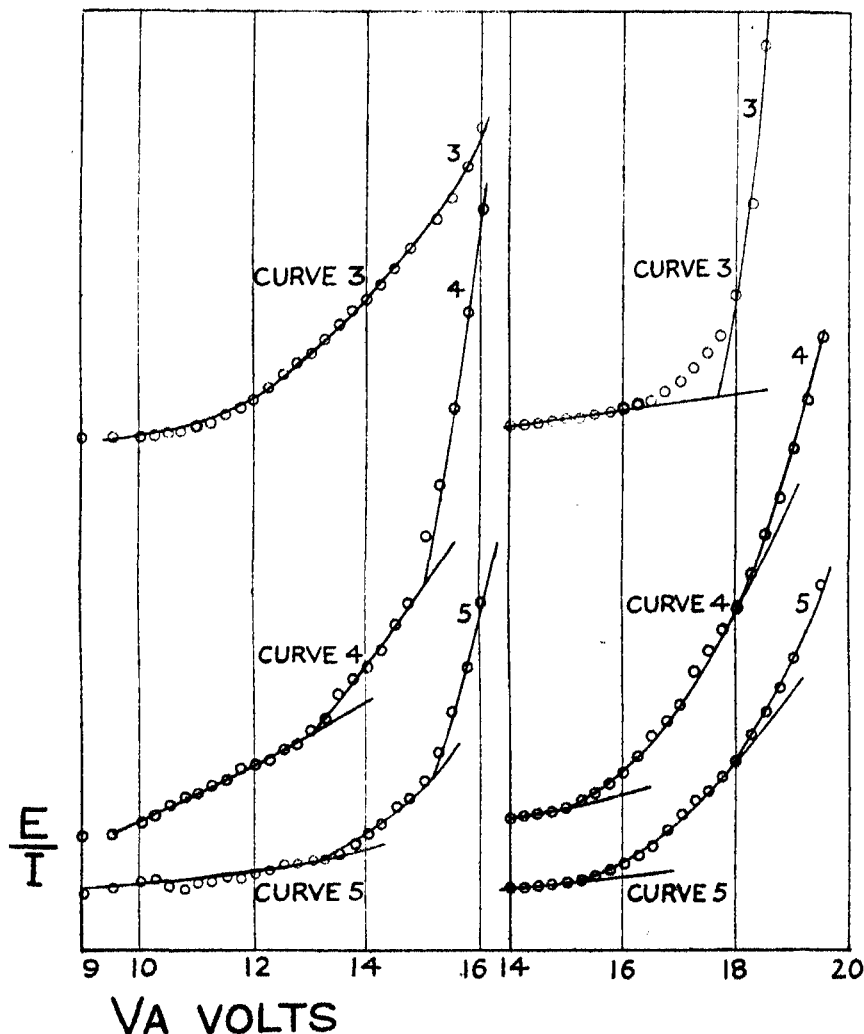


FIG. 3.—Ionisation and radiation.—Curve (3): Hydrogen at  $10^{-2}$  mm. (plain nickel target). Curve (4): Catalytic nickel and hydrogen at  $10^{-4}$  mm. Curve (5): Plain nickel and hydrogen at  $10^{-4}$  mm.

\* It was found that, presumably owing to impurities in the tungsten, the tungsten filament gave a copious positive ion emission. The oxide-coated filament was free from this defect, and also minimised the possibilities of thermal dissociation.

As one would expect, there is only one well-marked discontinuity, namely, the very strong one due to ionisation of the hydrogen molecule. This occurs at an observed voltage of 17.6 volts, indicating a correction of  $-1.6$  volts to be applied to all observed voltages in experiments with a nickel target. Curve (3) was obtained with plain nickel, but exactly similar curves were obtained with catalytic nickel; this was to be expected, since nearly all the effects observed at such a pressure must have been due to the body of gas between the filament and the target.\*

Curves (4) and (5) were obtained with catalytic and plain nickel respectively at a gas pressure of  $10^{-4}$  mm.; that is to say, under circumstances where the predominating effects originate in the gas at the metal surface. It is at once clear that the form of the curve is widely different from that obtained with plain molecular hydrogen. The strong breaks are observed at corrected voltages of  $(13.0 - 1.6)$ , or 11.4 volts, and at  $(15.0 - 1.6)$ , or 13.4 volts. A weaker break is observed near 18 volts, but the change of direction is so slight as to make exact location difficult, and the break most probably corresponds to the strong one at 17.6 volts in curve (3). In some of the unpublished curves this last break is almost impossible to detect at all, although the two lower breaks are just as well defined as ever.

The corrected voltages for the two lower breaks on a series of three curves for each target are given below:—

	Catalytic Nickel.	Plain Nickel.
First break .....	11.3, 11.3, 11.3	11.2, 11.4, 11.6
Second break .....	13.4, 13.4, 13.4	13.4, 13.4, 13.4

The observed facts are, then, that when conditions are changed by lowering the pressure so that the effects observed are due to hydrogen plus catalyst, rather than hydrogen alone, the 16-volt break due to molecular hydrogen almost disappears and is replaced by two breaks at 11.4 volts and 13.4 volts respectively, of which the latter is the stronger.

The 13.4-volt break can scarcely be other than that due to ionisation of the hydrogen atom. The interpretation of the 11.4-volt break is less simple. There are four possibilities: the break may be associated with the hydrogen molecule, with the hydrogen atom, with the nickel target, or with a hydrogen-

\* It will be observed that this hydrogen molecule break is not as sharp as the others. This would be expected because of electron distribution (Olmstead, 'Phys. Rev.', vol. 20, p. 623 (1922)), and also because the arrangement of the electrodes is such that ionisation can take place at any point in the path of the accelerated electron. When effects from the metal target are measured, on the other hand, all electrons fall through the same potential drop and hence the breaks are sharper.

nickel complex. The last two alternatives are ruled out by the fact that a break at about the same voltage occurs with a target of catalytic copper; that it is not associated with the target alone is also confirmed by the observation described below, that effects due to gas-free nickel are negligible compared with the currents measured in the above determinations. This leaves the two alternatives of the hydrogen molecule and the hydrogen atom. The fact that it does not appear in the high-pressure measurements suggests that it is not associated with the molecule. The break is almost certainly to be identified with that observed by Olmstead\* at the same voltage. Olmstead adduces evidence to show that the break is due to ionisation of the hydrogen molecule. Olmstead's curves, however, show that the 11.4-volt break does not appear in his "Grid off for Ionisation" curve (where dissociation is negligible), whereas it makes its appearance, together with the 13.4-volt break in the "Grid on for Ionisation" curve, where the incandescent grid is introduced to produce thermal dissociation of the hydrogen. It is significant that the "Grid off" (no dissociation) curve is closely similar to curve (3) of the present work, while the "Grid on" (thermal dissociation) curve is like curves (4) and (5).

Thus, whatever be the interpretation of the 11.4-volt break, it seems to be clearly indicated that the presence of nickel (both in the catalytic and unactivated condition) brings out strongly the ionisation potential of atomic hydrogen, and, in general, has a similar effect to that obtained by Olmstead in the use of an incandescent grid to produce thermal dissociation.

*Ionisation Measurements with Catalytic Copper.*—Similar experiments were carried out with copper, except that the absence of a plain copper target precluded any measurements with unactivated copper. However, the close similarity between catalytic and plain nickel suggested that experiments with plain copper would be superfluous. Determinations were therefore made with catalytic copper as a target at hydrogen pressures of  $10^{-2}$  and  $10^{-4}$  mm. respectively. Typical curves are shown in fig. 4.

Curve (6) was obtained at the higher pressure and shows one strong break at 18.6 volts, indicating a correction of  $-2.6$  volts to be applied to all observed voltages. Curve (7) was obtained at the lower pressure and shows breaks at corrected voltages of 11.4 and 13.3 volts with a much weaker effect at 16 volts. The figures for the location of the breaks on a series of three curves at each pressure are as follows (voltages being corrected):

\* 'Phys. Rev.', vol. 20, p. 613 (1922).

Pressure of  $10^{-2}$  mm.  
 No break observed at 11.4.  
 No break observed at 13.3.  
 16.1, 15.9 and 16.1.

Pressure of  $10^{-4}$  mm.  
 11.4, 11.3 and 11.4.  
 13.2, 13.2 and 13.4.  
 Break at 16, weak and difficult to locate exactly.

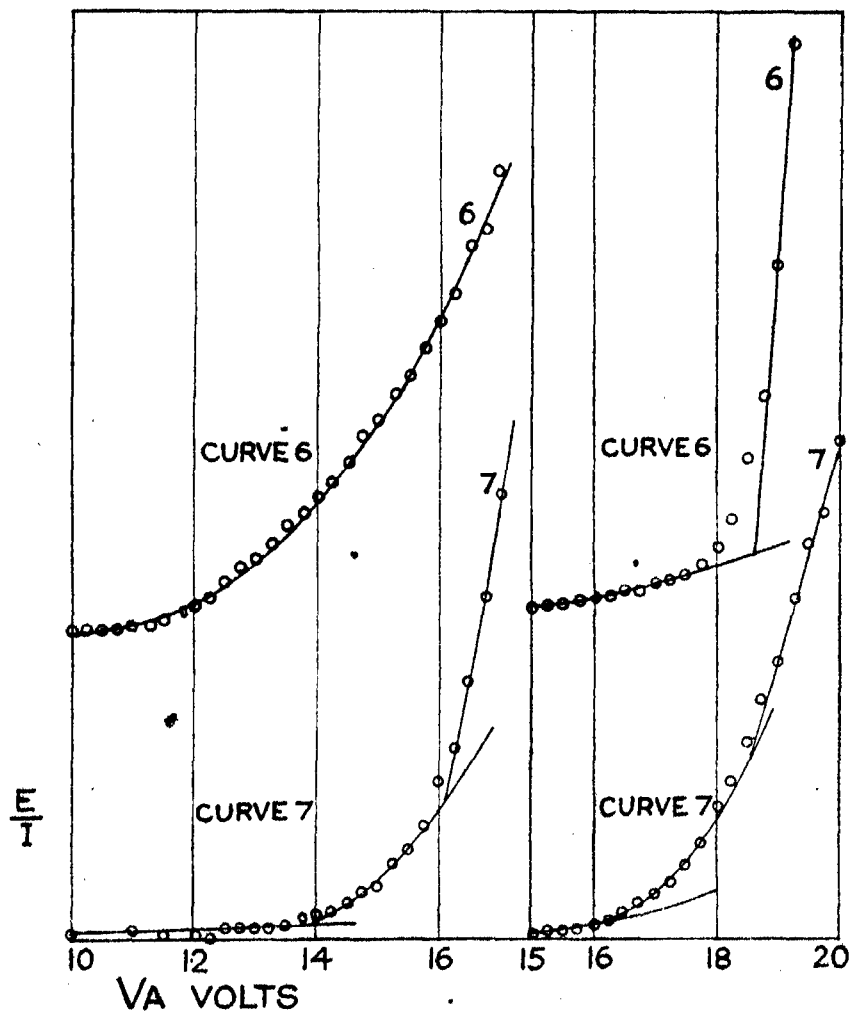


FIG. 4.

The results are thus closely similar to those obtained with catalytic and plain nickel, and suggest that in the case of catalytic copper also atomic hydrogen is present in appreciable quantity. It is reassuring to observe that,



in spite of the large initial velocity and contact potential correction, the position of the breaks agrees so closely with the observations in the case of nickel, where different corrections are applied.

*Evidence that the Effects observed at  $10^{-4}$  mm. Pressure are associated with Hydrogen at the Catalyst Surface.*—There are two pieces of evidence that, in experiments at  $10^{-4}$  mm. pressure, we are observing effects originating near the catalyst surface and not in the body of the gas. The first is the fact that the form of the current-voltage curve is so different at the lower pressure from that observed at the higher pressures. The second is afforded by comparing the ionisation current corresponding to a given voltage at  $10^{-4}$  mm. and at  $10^{-2}$  mm. pressure. If no surface effect were introduced at the lower pressure we should expect, on the same principle as that of the ionisation gauge, that current would be proportional to pressure. Observation showed, on the contrary, that the current at the lower pressure was anywhere from five to ten times that corresponding to pressure-proportionality. This was true of both plain and catalytic nickel and shows that in both cases a strong surface effect was being measured at the lower pressure.

*Evidence that the Metal of the Target Itself does not contribute appreciably to the Effects observed.*—Such a test was necessary to lend conclusiveness to the foregoing experiments. It had been found impossible to do a blank experiment of the kind described by Gauger, because in the presence of the adsorbent metal targets and the cold (and unbaked) copper butt-end, the last traces of gas were tenaciously retained and the necessary freedom from gas in the tube could not be obtained. The targets were therefore removed and the butt-end replaced by a disc of plain nickel supported on a thin nickel stem screwed into the brass-glass joint below. The target had been "de-gassed" by treatment in the induction furnace and the experimental tube was baked out for a longer period and at a higher temperature than the presence of heat-sensitive catalysts had previously permitted.

With such a target it was possible to measure the effects due to gas-free nickel alone. A run was carried out with no hydrogen admitted and with the gauzes arranged to measure radiation only. The much smaller currents observed were of such magnitude as to show that radiation from the target itself could not have made any appreciable contribution to the previous measurements.

#### *Discussion of Results.*

The series of experiments described above is a demonstration of the presence of atomic hydrogen in the systems comprised by hydrogen in contact with

catalytic nickel, plain nickel and catalytic copper respectively. The demonstration has several limitations. In the first place, it is only qualitative; strictly speaking, it tells us nothing of the proportion of atomic to molecular hydrogen in the adsorption layer, although the strength of the 13.4-volt break precludes the possibility of atomic hydrogen being present merely in minimal quantity. In the second place, the experiments do not exclusively correlate the presence of atomic hydrogen with catalytic activity. For this reason it was proposed to extend the experiments to a metal of very small catalytic activity like lead; it is regretted that circumstances prevented this.

If we assume such a correlation to exist, we have to explain the close similarity between the results obtained with plain and catalytic nickel. We might attribute it to the appreciable catalytic activity of plain nickel coupled with a possible partial de-activation of the catalytic nickel. In the absence of further experimental data, such speculation seems idle. One significant peculiarity of the critical potential method for exploring the catalyst surface should, however, be emphasised at this point. The electron bombardment method employed takes, as it were, a two-dimensional view of the catalyst, so that differences due to amount of surface as distinct from quality of surface are eliminated in the effects observed. This eliminates from our results one of the two factors governing catalytic activity as recorded by chemical observation.

The experiments, therefore, offer no conclusive hypothesis of catalytic action, but the presence of atomic hydrogen in the adsorption layer is probably of contributory significance in the light of such work as that of Taylor and Marshall.\*

#### *Summary.*

Several criticisms are advanced which seem to render invalid Gauger's measurements of the critical potentials of hydrogen in the presence of catalytic nickel.

A modified apparatus is described in which measurements of ionisation from hydrogen in the presence of catalytic nickel, plain nickel and catalytic copper were made. By comparison of these results with those obtained when molecular hydrogen was the preponderating source of ionisation, it is concluded that substantial quantities of atomic hydrogen are present at the metal surface in each of the three former cases. It is shown that a similarity exists between the effect upon the form of the ionisation curve of the presence of the catalyst metal and that of an incandescent grid (as determined by Olmstead). The

\* 'J. Phys. Chem.,' vol. 29, p. 1140 (1925).

results are of significance in connection with the mechanism of catalytic hydrogenation.

In conclusion, the author wishes to express his gratitude to Prof. K. T. Compton and Prof. H. S. Taylor for their constant encouragement, advice and assistance. He also welcomes the opportunity to thank all the research workers in Palmer Physical Laboratory, Princeton, whose friendly help was so generously given at all times.

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### *The Spectrum of Ionised Oxygen (O II).*

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(Received December 23, 1925.)

Two different line spectra of oxygen have long been known under the names "compound line" and "elementary line" spectra, assigned by Schuster in 1879\* on the supposition that complex and simplified molecules or "molecular groupings" were respectively involved in their production. The possibility of a further modification of the line spectrum was also foreshadowed by Schuster, in collaboration with Roscoe,† in the observation of a line at  $\lambda$  5592 when a condensed discharge was passed through oxygen in a short and narrow capillary tube. Additional lines of this third type were observed later by Lunt,‡ and further investigated by Fowler and Brooksbank.§

In accordance with present views as to the origin of spectra, the three spectra are attributed to neutral, singly-ionised, and doubly-ionised atoms, and are designated O I, O II, O III, or O,  $O^+$ ,  $O^{++}$ . Other spectra representing higher degrees of ionisation are theoretically possible, and evidence of the production of O IV and O V in the spectra of vacuum sparks has been obtained

\* 'Phil. Trans.,' vol. 170, p. 41 (1879).

† 'Mem. Phil. Soc. Manchester,' 3rd Series, vol. 7, p. 82 (1880).

‡ 'Annals of the Cape Observatory,' vol. 10, pt. II, p. 26b (1906).

§ 'Monthly Notices R.A.S.,' vol. 77, p. 511 (1917).

by Millikan and Bowen.\* The first three spectra are of considerable interest to astrophysicists on account of their occurrence in stars of successively higher temperatures, in strict accordance with the results of laboratory experiments. Among other points of interest, the analysis of these spectra may eventually lead to trustworthy values of the successive ionisation potentials, and thence to important deductions as to stellar temperatures. This result, however, has only at present been finally attained with respect to O I, through the extension of the observations into the extreme ultra-violet by Hopfield.†

Some of the regularities in the spectrum of O II have already been recognised by the present author‡ and by Croze,§ the latter partly with the aid of his earlier observations of the spectrum with the source in a magnetic field.||

The present paper gives the results of new measurements of the lines of O II in the region  $\lambda$  6750 to  $\lambda$  1950, together with details of the numerous additional regularities which have been traced. An extension to shorter wavelengths is contemplated, and the structure of the third spectrum is also under investigation.

#### *Observational Data.*

Lines attributed to O II are conspicuous in the ordinary spark in air, but under these conditions they are mostly too broad for accurate measurements. Most of the measurements have accordingly been made on photographs of the spectrum of the discharge in vacuum tubes, where the conditions could be so controlled as to produce a majority of the lines with the desired sharpness. The O II lines were produced by condensed discharges of moderate intensity through capillary tubes, and could be readily distinguished from the lines of O III, which were added to the spectrum as the pressure was lowered and the intensity of the discharge increased.

Several spectrographs were employed in the investigation, but all were of adequate dispersion and resolving power for the particular regions under examination with them. Thus, for the visual spectrum, most of the photographs were taken with a large Littrow glass spectrograph, giving a dispersion ranging from 10 Å per mm. at  $\lambda$  5900 to 1.9 Å per mm. at  $\lambda$  4000. For the

\* 'Phys. Rev.', Sept., 1924, p. 209. 'Proc. Nat. Acad. Sci., Washington,' vol. 11, p. 329 (1925).

† 'Astrophys. Journ.', vol. 59, p. 114 (1924).

‡ 'Report on Series in Line Spectra,' p. 167 (1922).

§ 'Comptes Rendus,' vol. 180, pp. 277 and 432 (1925).

|| 'Ann. de Physique,' vol. 1, p. 80 (1914).

ultra-violet, a large quartz spectrograph (Hilger's E 1) was employed, giving 12 Å per mm. at  $\lambda$  4000 and 2 Å per mm. at  $\lambda$  2300. Many measurements were also made on photographs taken in the first order of a 10-ft. concave grating, giving about  $5\frac{1}{2}$  Å per mm., and of many of the stronger lines on third order plates. For the region  $\lambda$  2280— $\lambda$  1850, a small quartz spectrograph by Bellingham and Stanley was used, giving 9.8 Å per mm. at  $\lambda$  2280 and 4.8 Å per mm. at  $\lambda$  1850.\*

Relative accuracy over moderate ranges, it may be remarked, is not difficult to obtain, but on account of the long exposures required to bring out some of the lines, and the consequent liability to displacements arising from temperature changes, the absolute values are less certainly reached. The analysis of the spectrum, however, provides a check on the values obtained for some of the lines. In view of the great labour required to establish wave-lengths to seven figures, most of them are given to six figures.

The wave-lengths of some of the stronger lines in the blue and violet had previously been determined with great care, under the present author's direction, by J. S. Clark.† With two exceptions these have been verified to at least the second decimal place, and have been used as standards for the measurement of fainter intermediate lines on some of the photographs.

An effort has been made to record the spectrum as completely as possible, because faint lines are frequently of importance for the completion of multiplet groups. Care has also been taken to exclude lines due to carbon or to oxygen at stages of ionisation higher than the first. Pending a more complete investigation of the various spectra of carbon, however, it is not quite certain that every line of this element has been eliminated.

#### *Description of Table I.*

The wave-lengths (international scale) of all the lines which are believed to be due to O II are collected in Table I. The figures in brackets following the wave-lengths in column 1 indicate approximate relative intensities in the usual manner. Lines which have a tendency to become diffuse are indicated by the letter *n* attached to the intensity number. A few groups of lines show a broadening and displacement towards the red under some conditions, and are distinguished by the letter *r*; the tabulated wave-lengths of such lines were determined from plates taken with the gas at moderate or low pressures.

\* The author is indebted to the Government Grant Committee for this instrument.

† 'Astrophys. Journ.,' vol. 40, p. 333 (1914).

The third and fourth columns of the table indicate the classification of the lines, as explained later. Next follow the observations of Exner and Haschek, Lunt and Schniederjost, and some of those by Eisig, as quoted by Kayser,\* but omitting lines which appear to belong to O III. These wave-lengths have been corrected to the international scale. In the earlier part of the table only the lines of Eisig which are not included by the other observers are noted. It will be observed that the number of lines attributed to O II has been greatly increased by the present observations.

Two groups of lines,  $\lambda$  3048— $\lambda$  2992 and  $\lambda$  2918— $\lambda$  2885, which have not yet been classified, are remarkable for their diffuseness in most of the photographs which have been obtained. Approximate measures of these lines in the diffuse state are given in the column of remarks, while those in the first column are of fairly well-defined lines in a particular photograph, which are believed to correspond with the diffuse lines.

An isolated narrow triplet in the ultra-violet has been omitted from the table, namely :—

$\lambda$		$\nu$	$\Delta\nu$
3218.04	(3)	31065.87	
			12.56
3216.74	(2)	31078.43	
			7.05
3216.01	(2)	31085.48	

The separations appear to be identical with those of two inverted triplets at  $\lambda\lambda$  6264 and 5410, which have been assigned by Runge and Paschen to O I.† The triplet is, therefore, probably due to O I, as is also a similar triplet in the extreme red,  $\lambda$  8221, observed by Merrill, Hopper and Keith.‡

The number of lines entered in the table, extending from the red to  $\lambda$  1956 in the far ultra-violet is about 400. Of these, 90 have been classed as belonging to the doublet system, and 68 to the quartet system, including the majority of the stronger lines, and many of the fainter ones. Further analysis of the data may be expected to lead to the recognition of other regularities.

\* 'Handbuch der Spectroscopie,' vol. VI, p. 214.

† Fowler's 'Report on Series,' p. 169.

‡ 'Astrophys. Journ.,' vol. 54, p. 76 (1921).

Table I.—Lines of Ionised Oxygen (O II, or O<sup>+</sup>).

$\lambda$ , Intensity.	$\nu$	Combinations.		Other Observations.		Remarks.
		Doublet.	Quartet.	Exner and Haschek.	Lunt.	
6721.35 (5)	14873.87	$2p_2-2s_1$				
6854.77 (1)	15022.68					
6640.90 (4)	15054.05	$2p_1-2s_1$				
5206.73 (5)	19200.58	$ap'_2-ap''_2$				Isolated group.
5190.56 (3)	19260.40	$ap'_1-ap''_2$				
5176.00 (2)	19314.57	$ap'_2-ap''_1$				
5160.02 (4)	19374.39	$ap'_1-ap''_1$				
4955.78 (3)	20172.84	$ap'_2-bd'_2$			5.83 (1)	$^2p' ^2d'$ identified by Croze.
4943.06 (7)	20224.76	$ap'_2-bd'_2$			3.27 (6)	
4941.12 (5)	20232.70	$ap'_1-bd'_2$			1.04 (4)	
4924.60 (6)	20300.57				4.77 (6)	
4906.88 (5)	20373.87				7.09 (5)	
4890.93 (4)	20440.31				0.87 (3)	
4871.58 (5)	20521.50	$bp'_2-cd'_2$			1.70 (4)	
4864.95 (3)	20549.47				5.10 (1)	
4861.03 (3)	20566.04	$bp'_1-cd'_2$			1.12 (3)	
4856.82 (3)	20583.38		$s_2-d'_{21}$		7.01 (4)	
4856.49 (2)	20585.27		$s_2-d'_2$			
4845.01 (1)	20634.04		$s_2-x_3$			
4843.26 (1n)	20641.50				4.26 (2d)	Possibly double.
4752.70 (2)	21034.81				2.96 (0)	
4751.34 (4)	21040.83				1.59 (4)	
4744.85 (0)	21069.61					
4741.71 (3)	21083.56				2.12 (3)	
4710.04 (5)	21225.31			10.1 (1)	09.79 (2)	
4705.36 (8)	21246.43			5.38 (2)	5.14 (6)	
4703.18 (3)	21256.28					Eisig 03.2 (1)
4701.76 (0)	21262.70	$bp'_2-bp''_1$				
4701.23 (2)	21265.10	$bp'_2-bp''_2$				Eisig 01.3 (1)
4699.21 (7)	21274.23			9.21 (2)	9.01 (5)	
4696.36 (2)	21287.15		$ap_2-d_2$			$^4p ^4d$ identified by Croze.
4691.47 (1)	21309.33	$bp'_1-bp''_1$				
4690.97 (0)	21311.60	$bp'_1-bp''_2$				
†4676.246 (8)	21378.70		$ap_2-d_2$	6.16 (2)	6.04 (5)	†= $\lambda$ Clark.
4673.75 (4)	21390.12		$ap_2-d_1$		3.71 (0)	
4669.53 (0)	21409.46					
†4661.650 (9)	21445.64		$ap_2-d_2$	1.58 (2)	1.46 (5)	
†4650.853 (6)	21495.43		$ap_1-d_1$	0.82 (2)	0.77 (5)	
†4649.148 (10)	21503.32		$ap_2-d_2$		8.88 (9)	
†4641.827 (9)	21537.23		$ap_2-d_2$	1.76 (3)	1.66 (8)	
†4638.865 (6)	21550.98		$ap_1-d_2$	8.81 (2)	8.70 (5)	
4610.14 (3n)	21685.27					
4609.42 (4n)	21688.65			9.55 (1)	9.22 (2)	
4602.11 (2n)	21723.11				2.20 (0)	
†4596.189 (8)	21751.08			6.13 (3)	5.87 (7)	} $\Delta\nu = 24.68$ .
†4590.983 (9)	21775.76			0.95 (3)	0.73 (8)	
4506.50 (2n)	22183.07					
4491.25 (3n)	22259.29				1.04 (0)	
4489.48 (1n)	22268.07					
4488.09 (2n)	22274.97					
4487.72 (0n)	22276.80					

Table I—continued.

$\lambda$ , Intensity.	$\nu$ .	Combinations.		Other Observations.		Remarks.
		Doublet.	Quartet.	Exner and Haschek.	Lunt.	
4477.88 (2n)	22325.75					
4469.32 (3)	22368.51			9.38 (1)	9.31 (2)	
4467.88 (4)	22375.72			7.89 (2)	7.71 (3)	
4467.55 (1)	22377.37					
4466.32 (2n)	22383.54					
4465.40 (4)	22388.14			5.37 (2)	} 5.80(4d)	Eisig 66.5 (1). $2p^3d$ identified by Croze.
4452.38 (6)	22453.62			2.40 (2)	2.24 (3)	
4448.21 (6)	22474.66				8.10 (3)	
4447.08 (1)	22480.37					
4443.05 (5)	22500.76			3.12 (1)	3.01 (2)	
†4416.974 (8)	22633.60	$2p_1-ad_3$		6.97 (5)	6.85 (9)	† = $\lambda$ Clark.
†4414.888 (10)	22644.29	$2p_2-ad_3$		4.90 (8)	4.91 (10)	
4406.02 (1)	22689.86	$ad_3-bd'_3$				
4395.95 (7)	22741.84	$ad_3-bd'_3$		5.97 (2)	5.87 (3)	
4379.55 (2n)	22827.00					
4378.40 (3n)	22833.00					
4376.15 (0n)	22844.74					
4371.05 (2n)	22868.25					
4369.28 (4)	22880.66	$ad_2-bd'_2$		9.31 (1)	9.19 (2)	
†4366.906 (7)	22893.09		$ap_2-p'_2$	6.87 (3)	6.86 (6)	$4p^4p'$ identified by Croze.
4359.38 (1)	22932.62	$ad_3-bd'_3$				
4358.40 (0)	22937.77					
4357.25 (0)	22943.83					
4353.60 (1n)	22963.06					
†4351.275 (6)	22975.33	$ad'_3-bd_3$		1.37 (3)	1.18 (7)	
†4349.435 (8)	22985.05		$ap_3-p'_3$	9.41 (6)	9.36 (8)	
†4347.429 (5)	22995.66	$ad'_3-bd_3$		7.42 (2)	7.38 (6)	
†4345.570 (7)	23005.50		$ap_2-p'_1$	5.55 (3)	5.59 (6)	
4344.42 (0n)	23011.58					
4343.30 (00)	23017.52					
4342.00 (4n)	23024.42				1.85 (3)	
4340.36 (2n)	23033.11				0.34 (2)	
4336.86 (6)	23051.70		$ap_2-p'_2$	6.85 (2)	6.75 (3)	
4334.29 (0n)	23065.4					
4332.76 (1n)	23073.51					
4331.89 (2)	23078.15	$bd_2-cd'_2$			1.80 (0)	
4331.47 (0)	23080.38	$bd_2-cd'_3$				
4331.21 (0n)	23081.8			1.07 (1)		
4328.62 (2)	23095.58	$bp'_2-bs'_1$		8.54 (1)	8.72 (0)	
4327.89 (0)	23099.47	$bd_3-cd'_3$				
4327.48 (3)	23101.66	$bd_3-cd'_3$		7.45 (1)	7.42 (2)	
4325.77 (3)	23110.80		$ap_1-p'_1$	5.69 (1)	5.74 (1)	
4319.93 (1)	23142.04	$bp'-bs'_1$				
†4319.647 (8)	23143.55		$ap_2-p'_2$	9.62 (3)	9.63 (6)	$\lambda$ approx.
†4317.160 (8)	23156.88		$ap_1-p'_2$	7.11 (3)	7.09 (6)	
4315.55 (0n)	23165.53					
4313.43 (1n)	23176.91					
4312.10 (0n)	23184.06					
4308.96 (1n)	23200.95					
4307.31 (1n)	23209.84					
4305.53 (0)	23219.54					
4303.82 (5n)	23228.66			3.58 (1n)	3.61 (3)	
4303.00 (0n)	23233.09					



Table I—continued.

$\lambda$ , Intensity.	$\nu$ .	Combinations.		Other Observations.		Remarks.
		Doublet.	Quartet.	Exner and Haschek.	Lunt.	
4294.82 (3n)	23277.34				4.89 (2)	
4292.23 (0n)	23291.38				2.27 (0)	
4291.25 (1n)	23296.70				1.29 (1)	
4288.83 (1n)	23309.85				8.86 (0)	
4285.70 (3n)	23326.87				5.72 (1)	
4283.75 (0n)	23337.50				3.65 (0)	
4282.96 (1n)	23341.80				3.05 (0)	
4281.40 (0n)	23350.30					
4277.90 (1n)	23369.40					
4277.40 (1n)	23372.13				7.70 (0)	
4276.71 (1n)	23375.92				6.72 (1)	
4275.52 (4n)	23382.40				5.61 (3)	
4273.17 (0n)	23395.27					
4253.98 (8n)	23500.80			3.58 (1n)	4.08 (4)	
4196.72 (1)	23821.44	$bd_3 - bp''_1$ $bd_3 - bp''_2$			6.72 (0)	
4192.50 (2)	23845.42				2.60 (0)	
†4189.793 (10)	23860.82			9.90 (7)	9.92 (8)	$\Delta\nu = 24.75$ .
†4185.453 (8)	23885.57			5.56 (6)	5.54 (8)	
4169.23 (4)	23978.50			9.33 (2)	9.27 (3)	
4156.54 (3)	24051.70			6.67 (1)	6.60 (1)	
†4153.310 (7)	24070.42				3.48 (6)	
4146.09 (3)	24112.33				6.15 (3)	
4145.90 (0)	24113.44					
4143.77 (2)	24125.84			3.74 (1)	3.79 (3)	
4143.52 (1)	24127.29					
4142.24 (0)	24134.74					
4142.00 (1)	24136.14			2.21 (1)	2.22 (2)	
4140.74 (0)	24143.49					
4132.82 (6)	24189.74			2.87 (2)	2.91 (5)	32.99 Clark ("unsatisfactory").
4129.34 (2)	24210.14			9.45 (1)	9.47 (0)	
4121.48 (4)	24256.31			1.58 (2)	1.49 (2)	
4120.55 (2)	24261.78		$p'_3 - d'_2$			$p'_4 d'$ partially identified by Croze. 20.267 Clark.
			$p'_3 - d'_3$	0.47 (3)	0.46 (6)	
4120.30 (3)	24263.25		$p'_3 - d'_4$	9.31 (8)	9.36 (8)	
†4119.222 (8)	24269.61			4.05 (1)	3.92 (0)	
4113.82 (1)	24301.48			2.11 (2)	2.07 (3)	
4112.04 (4)	24312.00		$p'_3 - x_2$	0.91 (2)	0.80 (3)	
4110.80 (3)	24319.33					
4110.20 (1)	24322.88					
4108.75 (0n)	24331.48					
4107.07 (1n)	24341.41				7.12 (0)	
4106.03 (0)	24347.57		$d_3 - f_2$			$d'_4$ partially identified by Croze.
†4105.001 (7)	24353.68		$p'_3 - d'_1$			
4104.74 (5)	24355.24		$p'_3 - d'_2$	5.00 (5)	5.00 (6)	
4103.01 (5)	24365.51				3.09 (2)	
4098.27 (0n)	24393.68				8.28 (1)	
4097.32 (1)	24399.34		$p'_1 - d'_1$			
4097.25 (4n)	24399.76		$p'_1 - d'_2$		7.28 (4)	
4096.54 (3)	24403.98		$p'_1 - x_2$		6.50 (2)	
4095.63 (0n)	24409.40				5.76 (1)	
4094.18 (0)	24418.05		$d_3 - f_2$			
4092.94 (5)	24425.45		$d_3 - f_4$	3.00 (3)	2.96 (4)	

Table I—continued.

$\lambda$ , Intensity.	$\nu$ .	Combinations.		Other Observations.		Remarks.
		Doublet.	Quartet.	Exner and Haschek.	Lunt.	
4089.28 (4n)	24447.31			9.08 (2)	9.28 (5)	
4087.16 (2n)	24459.98				7.18 (2)	
4085.12 (3)	24472.20		$d_3-f_3$	5.21 (3)	5.17 (5)	
4084.66 (1)	24474.95				4.01 (2)	
4083.90 (2n)	24479.51					
4079.00 (0)	24508.91					
4078.86 (4)	24509.74		$d_2-f_2$	8.96 (2)	8.86 (4)	
†4075.869 (10)	24527.74		$d_4-f_5$	5.93 (10)	5.94 (10)	† = $\lambda$ Clark.
†4072.156 (8)	24550.11		$d_3-f_4$	2.25 (10)	2.30 (10)	
4071.20 (0)	24555.88					
†4069.903 (6)	24563.70		$d_2-f_3$	} 9.89 (10)	9.92 (10)	.
†4069.635 (4)	24565.31		$d_1-f_3$			
4062.90 (1n)	24606.04				3.08 (0)	
4060.98 (2n)	24617.67				0.92 (1)?	
4060.58 (3n)	24620.09					
4054.60 (0n)	24656.41					
4048.22 (1n)	24695.26				8.40 (0)	
4041.20 (0n)	24738.16					
4035.00 (0n)	24776.17					
4026.40 (0n)	24829.09					
4024.04 (1n)	24843.65					
4021.90 (0n)	24856.87					
3985.37 (0)	25084.70					
†3982.725 (5)	25101.37	$2p_2-ap'_1$		2.75 (2)	2.78 (6)	$2p^2p'$ identified by Croze.
†3973.266 (10)	25161.12	$2p_2-ap'_2$		3.29 (8)	3.36 (9)	
3967.44 (1)	25198.07					
963.13 (0)	25225.46					
†3954.368 (7)	25281.36	$2p_1-ap'_1$		4.40 (4)	4.49 (7)	
3945.050 (5)	25341.10	$2p_1-ap'_2$		5.10 (3)	5.11 (6)	45.033 Clark.
3919.279 (6)	25507.70	$ad'_2-bp'_1$			9.36 (6)	3rd order grating.
3912.088 (2)	25554.59	$ad'_3-bp'_2$				" "
†3911.951 (10)	25555.48	$ad'_3-bp'_3$		2.05 (3)	2.04 (7)	" "
3907.45 (4)	25584.92			7.58 (1)	7.49 (0)	
3896.30 (1)	25638.13					
3893.53 (2)	25677.05					
3883.15 (3)	25745.02		$d_4-d'_3$		3.16 (0)	$d^4d'$ partially identified by Croze.
3882.45 (1)	25749.66					
†3882.194 (7)	25751.37		$d_4-d'_4$	2.32 (3)	2.22 (6)	
3875.82 (4)	25793.70		$d_4-x_3$			
3874.10 (2)	25805.16					
3872.45 (1)	25816.15					
3864.68 (1)	25868.06		$d_2-d'_1$			
3864.45 (6)	25869.59		$d_2-d'_2$	4.59 (1)	4.55 (1)	
3863.50 (2)	25875.96		$d_2-d'_3$	3.55 (1)	3.56 (0)	
3857.18 (4)	25918.35		$d_2-d'_4$		7.22 (0)	
3856.16 (5)	25925.21		$d_2-x_3$		6.19 (0)	
3851.58 (2)	25956.05			} 1.35 (1)	1.03 (0)	
3851.04 (3)	25959.69		$d_2-d'_{21}$			
3850.81 (2)	25961.22		$d_2-d'_3$			
3847.89 (3)	25980.92			8.03 (1)		
3843.58 (3)	26010.05		$d_4-x_3$			
3842.82 (3)	26015.20		$d_1-d'_{21}$			

Table I—continued.

$\lambda$ , Intensity.	$\nu$ .	Combinations.		Other Observations.		Remarks.
		Doublet.	Quartet.	Exner and Haschek.	Lunt.	
3838.41 (0)	26045.10					N ?
3833.10 (3)	26081.18					
3830.45 (4r)	26099.22	$ap'_2-3p_1$				The lines marked r are sometimes broadened and displaced towards the red.
3821.68 (4r)	26159.10	$ap'_1-3p_1$			3.01 (0)	
3803.14 (6r)	26286.63	$ap'_3-3p_2$				
3794.48 (3r)	26346.52	$ap'_1-3p_2$				
3785.01 (0n)	26412.53					
3777.60 (4r)	26464.35		$s_2-hp_1$			
3762.63 (5r)	26569.63		$s_2-hp_2$		2.47 (0)	
3749.49 (9)	26662.74		$ap_3-s_2$	9.51 (5)	9.48 (7)	*p's identified by Paschen.
3740.77 (0)	26682.10					
3741.82 (0n)	26717.40		$s_2-hp_3$		9.80 (0)	
3739.92 (6r)	26730.98	$bp'_3-dd'_{32}$				
3735.94 (3)	26759.43					
3732.07 (0)	26787.20	$bp'_1-dd'_{32}$				
3729.34 (2)	26806.78		$ap_2-s_2$	7.32 (4)	7.34 (6)	
3727.33 (8)	26821.26		$ap_1-s_2$	2.80 (2)	2.72 (5)	
3712.75 (7)	26926.68					
3533.97 (00n)	28288.7					
3516.92 (0n)	28425.9					
3506.02 (0n)	28514.2					
3501.67 (00n)	28549.7					
3500.5 (00n)	28559.2					
3496.32 (2)	28593.35					
3495.44 (0n)	28600.5					
3494.66 (00n)	28606.9					
3468.23 (1)	28659.66					
3485.45 (0n)	28682.5					
3478.48 (0n)	28740.4					
3474.94 (1)	28769.27					
3470.81 (8)	28803.60	$ad_3-3p_2$		0.93 (1) ?		
3470.42 (5)	28806.74	$ad_2-3p_1$				
3459.07 (0n)	28901.2					
3457.99 (1n)	28910.3					
3453.81 (0n)	28949.4					
3447.98 (5)	28994.21	$ad_2-3p_2$				
3420.61 (3n)	29226.21					
3419.87 (2n)	29232.53					
3409.84 (6r)	29318.50	$bd_3-dd'_{32}$			Eisig. 10.1 (2)	} Sometimes broadened and displaced toward red.
3407.38 (7r)	29339.68	$bd_2-dd'_{32}$			7.6 (2)	
3390.25 (8)	29487.92	$s_1-ap''_2$		0.29 (2n)	0.1 (4)	
3377.20 (7)	29601.86	$s_1-ap''_1$		7.19 (1)	7.0 (3)	
3375.77 (0)	29614.4					
3374.77 (00)	29623.2					
3371.85 (2n)	29648.8					
3370.23 (00n)	29663.1					
3367.00 (00n)	29691.5					
3360.15 (00n)	29752.0					
3306.60 (6r)	30233.87		$p'_3-hp_1$			The whole group from 3306 to 3270 is sometimes broadened and displaced towards the red.
3305.15 (6r)	30247.13		$p'_3-hp_2$			
3301.56 (3r)	30280.03		$p'_1-hp_1$			
3295.13 (4r)	30339.12		$p'_3-hp_2$			
3290.13 (5r)	30385.22		$p'_1-hp_2$			

Table I—continued.

$\lambda$ , Intensity	$\nu$ .	Combinations.		Other observations.		Remarks.
		Doublet.	Quartet.	Exner and Haschek.	Eisig.	
3287.59 (9r)	30408.68		$p'_2-bp_3$		7.7 (1)	
3277.69 (7r)	30500.53		$p'_2-bp_3$			
3273.52 (7r)	30539.39				3.8 (1)	
3270.98 (7r)	30563.09				1.1 (1)	
3194.9 (00)	31200.9					
3189.2 (1n)	31544.6					
3165.1 (1n)	31585.5					C ?
3139.77 (4r)	31840.27		$d_3-bp_1$	9.32 (1)		All the lines of this group are sometimes broadened and displaced towards the red.
3138.44 (8r)	31853.78		$d_3-bp_2$		8.5 (1)	
3134.82 (10r)	31890.56		$d_4-bp_3$	5.2 (1)	4.8 (2)	
3134.32 (3r)	31895.64		$d_1-bp_1$			
3129.44 (7r)	31945.37		$d_2-bp_2$			
3124.02 (2r)	32000.82		$d_1-bp_3$			
3122.62 (6r)	32015.14		$d_3-bp_3$			
3113.71 (1r)	32106.75		$d_2-bp_3$			
3097.49 (1n)	32274.9					
3081.46 (2n)	32442.8					
*3048.0 (0)	32799.0					3048.0* (see footnote).
3039.76 (1)	32887.8					3040.0
3039.51 (1)	32890.5					3032.4
3032.50 (1)	32906.5					3029.0
3032.08 (2)	32971.1					3026.0
3028.82 (1)	33000.6					3016.0
3025.75 (1)	33040.1					3013.7
3015.87 (1)	33148.3					3010.0
3014.50 (1)	33163.3					Also O III here.
3013.37 (3)	33175.8					3008.8
3012.83 (1)	33181.7					3007.1
3009.83 (1d)	33214.8					3006.0
3008.77 (3)	33226.6					3003.0
3008.28 (1)	33232.0					2997.7 also O III here.
3007.08 (3)	33245.2			07.30 (2n)		2996.1
3006.82 (3)	33248.1					2992.5* Also C line here.
3006.04 (2)	33256.7					
3005.62 (2)	33261.4					
3002.93 (1)	33291.1					
2997.70 (3)	33340.2					
2995.89 (1)	33369.4					
*2992.56 (3)	33406.5					
2942.88 (2n)	33970.4					
§2915.65 (1n)	34287.7			Schnieder-jost.		2915.7§ (see footnote).
2911.76 (3n)	34333.5					2911.9
2911.14 (2n)	34340.8					O ?
2908.74 (1n)	34369.1					2908.8
2906.56 (4n)	34394.9					2906.6
2905.00 (2n)	34413.4					2905.3
2904.30 (2n)	34421.7					2904.2
2900.30 (0n)	34469.1					2900.4
2897.53 (1n)	34502.1					2897.7
2893.62 (2n)	34548.7					2893.4

Table I—continued.

$\lambda$ , Intensity.	$\nu$ .	Combinations.		Other Observations.		Remarks.
		Doublet.	Quartet.	Schnieder- jost.	—	
2887.85 (3n) 2885.90 (1n) 2883.78 (3)	34617.7 34641.1 34666.6					2888.0 2885.98 Assigned to O I by Pas- chen.
2878.95 (2) 2876.30 (1n) 2836.34 (2) 2808.78 (2n) 2800.01 (1n) 2783.07 (1n)	34724.8 34756.7 35246.4 35592.1 35703.7 35921.0			8.77 (2)  8.99 (1) 2.96 (1)		
2747.46 (6) 2733.34 (10)	36386.52 36574.47	$2s_1-3p_1$ $2s_1-3p_2$		3.08 (4)		} Isolated pair.
2718.84 (2) 2715.38 (3)	36769.5 36816.4	$as'_1-bp'_1$ $as'_1-bp'_2$		8.80 (1) 5.14 (2)		
2693.5 (0n) 2690.3 (0n)	37115 37159					
2575.443 (1) 2575.300 (6) 2571.476 (4)	38816.65 38818.80 38876.54	$ap'_2-cd'_2$ $ap'_2-cd'_3$ $ap'_1-cd'_2$		5.04 (3) 1.31 (2)		} Isolated pair.
2530.30 (5) 2527.03 (1) 2526.89 (4) 2523.23 (3) 2523.09 (1) 2517.97 (4)	39509.1 39560.2 39562.4 39619.8 39622.0 39702.6	$ap'_2-bp'_1$ $ap'_2-bp'_2$ $ap'_1-bp'_1$ $ap'_1-bp'_2$		0.14 (2) 6.75 (2) 2.98 (1) 7.80 (1)		
2445.55 (10) 2444.26 (5) 2441.06 (1n) 2436.10 (4n) 2433.56 (9)	40878.2 40899.8 40954.3 41036.8 41079.6	$2p_2-bd_2$ $2p_2-bd_3$  $2p_1-bd_2$		5.46 (4) 4.15 (3)  5.97 (2) 3.52 (3)		XH 45.47 (1), E 45.5 (3)
2425.62 (5n) 2418.80 (1) 2418.48 (6) 2415.13 (3) 2411.64 (3n) 2407.49 (4) 2407.37 (1) 2406.41 (3n)	41214.0 41333.7 41335.7 41393.0 41452.9 41524.4 41526.5 41543.0	$ad_2-cd'_2$ $ad_2-cd'_3$ $ap'_2-bs'_1$ $ap'_1-bs'_1$ $ad_2-cd'_2$ $ad_2-cd'_3$		5.47 (2) 8.51 (3) 5.02 (1) 1.52 (1) 7.38 (2)		XH 19.62
2375.73 (4) 2365.15 (3) 2365.03 (1)	42079.5 42267.7 42269.9	$ad_2-bp'_2$ $ad_2-bp'_1$ $ad_2-bp'_2$		5.64 (2) 5.07 (2)		
2339.38 (2) 2331.13 (oo) 2327.97 (2n) 2326.00 (1n) 2324.83 (on) 2322.14 (2n)	42733.3 42884.5 42942.7 42979.0 43000.7 43050.5			9.27 (1) 7.97 (1) 6.01 (1) 4.83 (1) 2.13 (1)		

Table I—continued.

$\lambda$ , Intensity.	$\nu$ .	Combinations.		Other Observations.		Remarks.
		Doublet.	Quartet.	Schnieder- jost.	—	
2319.66 (4n)	43096.5			9.64 (2)		
2316.76 (2n)	43150.5			6.74 (1)		
2316.10 (3n)	43102.7			6.13 (1)		
2313.06 (2n)	43219.5			3.08 (1)		
2307.72 (1n)	43319.5					
2302.82 (5)	43411.6	$2p_2-bp'_1$		2.82 (1)		
2300.35 (8)	43458.2	$2p_2-bp'_2$		0.35 (2)		
2293.32 (6)	43591.5	$2p_1-bp'_1$		3.34 (2)		
2290.86 (4)	43638.2	$2p_1-bp'_2$		0.82 (1)		
		*				
2284.88 (3)	43752.5			4.71 (1)		This and following wave-lengths are provisional.
2283.48 (2)	43779.3			3.43 (1)		
2262.80 (1)	44170.3	$ap'_2-4p_1$				
2259.77 (2)	44238.6	$ap'_1-4p_1$				
2252.90 (3)	44373.4	$ap'_2-4p_2$		2.8 (1)		
2250.00 (1)	44430.6	$ap'_1-4p_2$				
2195.70 (2)	45529.3					
2191.66 (1)	45613.2					
2190.66 (2)	45634.0					
2189.51 (1)	45657.9					
2186.22 (0)	45724.7					
2182.72 (4)	45799.9					
2161.65 (0)	46246.4					
2160.52 (0)	46270.6					
2148.50 (0)	46529.4					
2132.05 (5)	46888.3	$\begin{cases} ad_2-4p_2 \\ ad_2-4p_1 \\ ad_2-4p_2 \end{cases}$				
2123.39 (1)	47079.7					
2101.30 (4)	47574.4	$ad_2-dd'_2$				
2100.21 (0)	47599.1					
2092.90 (2)	47765.3	$ad_2-dd'_1$				
2075.15 (4)	48173.7					
2074.32 (1)	48193.0					
2072.23 (6)	48241.8					
2022.83 (1)	49419.6					
2021.45 (1)	49453.3					
2020.44 (2)	49478.0					
2020.27 (2)	49482.2					
2016.60 (2)	49572.4					
1963.61 (0)	50910.0					
1963.20 (2)	50920.6					
1961.60 (3)	50962.2					
1959.70 (1)	51011.6					No additional lines of O II noted as far as $\lambda$ 1850.
1956.78 (0)	51087.7					

\* Lines of the group extending from  $\lambda$  3048 to  $\lambda$  2992 are extremely diffuse on most of the photographs. Measurements in the first column are from a photograph taken at very low pressure; lines of Si, C and O III have been eliminated as far as possible, and it is believed that the wave lengths tabulated correspond with the estimates of the positions of the very diffuse lines indicated in the column of remarks.

§ The group  $\lambda$  2915 to  $\lambda$  2783 is similar in character to the group beginning at  $\lambda$  3048.

*Structure of the Spectrum.*

In accordance with recent developments in the analysis of spectra, the spectrum of O I has been found to be built up from triplet and quintet terms. In a discussion of Hopfield's observations it has been shown by Laporte\* that the supposed "doublet" system first traced by Runge and Paschen is in reality a triplet system, and is directly associated with the new set of triplets of short wave-lengths discovered by Hopfield; while the system previously supposed to consist of triplets is based upon quintet terms. From the position of oxygen in the periodic table, a septet system might also have been expected, but such terms have not yet been identified, and it seems possible that in elements of low atomic numbers lines depending upon the higher possible multiplicities are either weak or missing.

The spectrum of ionised oxygen (O II) was similarly expected to be built up from terms of doublet and quartet, and possibly sextet systems. Six pairs of lines having the separation  $\Delta\nu = 179\cdot9$  noted by the present writer were the first evidence of a probable doublet system, and a quartet system of terms was first indicated by Paschen's observations of the Zeeman effect† in three lines of O II at  $\lambda\lambda 3712\cdot8, 3727\cdot3, 3749\cdot5$ . The work of Croze, to which reference has already been made, considerably elucidated the general structure of the spectrum by the identification of several doublet and quartet combinations. These results are included in the present paper, in some cases with further details resulting from the use of greater resolving power and more accurate measurements.

*Notation.*

In view of the lack of uniformity in spectroscopic notation, it is necessary to explain the system which has been adopted in the present paper. This is merely an adaptation of the generalised notation of Landé, in which the characteristics of a term are completely specified by  $n^r_{kj}$ , where  $k$  and  $j$  respectively represent the azimuthal and inner quantum numbers, and  $r$  is the maximum multiplicity in the group to which the term belongs. In practice  $n_k$  is replaced by a term symbol such as  $ms, mp, md, mf, \dots$ , it being understood that the values of  $k$  for  $s, p, d, f, \dots$  are 1, 2, 3, 4,  $\dots$  respectively. For a Rydberg sequence the individual terms are indicated by successive numerical values of  $m$ . Only one probable sequence, however, has yet been recognised

\* 'Die Naturwissenschaften,' 12 Jahrg., Heft 29 (1924).

† Quoted by Landé, 'Zeit. f. Phys.,' vol. 15, p. 196 (1923).

in the spectrum of O II, and in other cases, when more than one term of the same type appears, the largest is designated by the prefix *a*, the second largest by *b* and so on. Terms of the same type are, of course, recognised as such by the structures of the multiplet combinations in which they appear, or by Zeeman effects.

The group multiplicity is indicated by an index on the upper left side of the term symbol; for example,  $a^2d$  (to be read as "*a* doublet *d*") denotes the largest *d* term identified in the doublet system, and  $b^4p$  (to be read as "*b* quartet *p*") the second largest in the quartet system.\* The multiplicity figures, however, are omitted when there is no possibility of ambiguity.

The components of double or multiple terms are indicated in the usual way by subscripts on the right of the term symbols. In the present paper the subscripts adopted are the inner quantum numbers (*j*), as these would now appear to be more convenient than the older system, especially in connection with the higher multiplicities. Combinations are ordinarily restricted to those in which  $\Delta j = \pm 1$  or 0, with the exclusion of the transition  $0 \rightarrow 0$ .

Besides the terms of ordinary types there are others which have been called "*gestrichene*," "primed" or "dashed" terms, and have been represented by  $\bar{p}$ ,  $\bar{d}$ , . . . ., or  $p'$ ,  $d'$ , . . . ., such terms being probably associated with the simultaneous displacement of two electrons. The form  $p'$ ,  $d'$ , . . . . has been adopted in the present paper. Such terms are subject to the usual rules in regard to combinations among themselves, and the combinations show the same kinds of multiplets and the same Zeeman effects as those of corresponding ordinary terms. In their intercombinations with the ordinary terms, however, they follow the rule  $\Delta k = 0$ , and  $\Delta k = \pm 1$  is forbidden; there is evidence also that the "primed" terms may combine with ordinary terms when  $\Delta k = \pm 2$ , as, for example,  $sd'$ , the usual restrictions as to inner quantum numbers being observed.

In the spectra of the alkaline earths, Russell and Saunders† have found additional terms which generally combine in the same manner as terms of ordinary types, but differ from them in not forming part of the regular Rydberg series; for such terms they have suggested the use of doubly-accented letters, as  $p''$ ,  $f''$ . In the spectrum of O II there are two terms which have been provisionally placed in this class, namely,  $ap''$ ,  $bp''$ .

\* Compare Russell & Saunders, 'Astrophys. Journ.,' vol. 61, p. 66 (1925).

† *Loc. cit.*



*Term Values.*

The investigation of the structure of the spectrum was carried on in the first instance by adopting an arbitrary value for one of the terms of the doublet system, and another for a term of the quartet system. Afterwards, it appeared probable that three of the doublet  $p$  terms formed part of a Rydberg sequence, while two others could be considered to be of the  $p''$  type as defined by Russell and Saunders. The three  $p$  terms in question are represented by the formula

$$mp_2 = 4R/[m + 0.316331 - 0.310848/m]^2,$$

giving

$$2p_2 = 93952.53$$

$$3p_2 = 42504.63$$

$$4p_2 = 24419.23$$

Although these values cannot yet be considered to be firmly established, they have been adopted in the tables for the doublet system which follow, and the remaining terms have been derived from the various combinations. These will at least serve the same purpose as values depending upon the assignment of an entirely arbitrary value to one of the terms.

In this connection it may be remarked that if the suggested Rydberg  $p$  sequence be justified, it seems possible that  $1s$  will be found to be the largest term of the doublet system. The value of  $1p_2$  indicated by the formula is 433942, which is quite improbably large for any term of the O II spectrum. On the other hand, the above values for  $2p$  lead to 79078.69 for the term  $2s$ , and the corresponding value of  $1s$  given by a simple Rydberg formula is 238,816. While this extrapolated term may be greatly in error, it represents an ionisation potential for O II of 29.5 volts, which is not hopelessly inconsistent with the 31 volts deduced from the discussion of stellar spectra.\*

A further test of the proposed term values may be expected from observations in the extreme ultra-violet, particularly through the combination  $1^2s-2^2p$ , but the available lists of oxygen lines in this region are not sufficiently detailed to provide a final test. It is, of course, possible that the deepest energy level may be represented by a term of the quartet system, but the quartet terms so far identified give no definite indications on this question.

[*Note added February 5, 1926.*—In a paper which has been published since the above was written ('Phil. Trans.,' A, vol. 225, p. 394) Mr. J. A. Carroll has quoted a list of oxygen lines measured by Bowen in the extreme ultra-

\* R. H. Fowler and E. A. Milne, 'Monthly Notices R.A.S.,' vol. 84, p. 499 (1924); Miss C. Payne, 'Harvard Coll. Obs. Circ.,' No. 256 (1924).

violet, which includes two lines at  $\lambda\lambda$  625·84, 625·14 not previously resolved. The wave-numbers of these lines are 159785·2, 159964·2, and their separation, 179·0, is identical with that of the terms  $2p_1$  and  $2p_2$  within the limits of error. If these lines be taken as  $1s-2p_1$  and  $1s-2p_2$  of O II, the value of  $1s$  becomes 253917, and would represent an ionisation potential of 31·35 volts, in close agreement with the astrophysical estimate.

Some doubt as to this interpretation, however, arises from the presence of another line at  $\lambda$  624·61 ( $\nu = 160099\cdot9$ ), which may possibly form a triplet with the two lines in question. If so, the three lines might be assignable to O III, for which Bowen and Millikan have already identified two triplets having somewhat similar separations. Details of these, using the wave-lengths quoted by Carroll, are as follows :

$\lambda$	$\nu$	$\Delta\nu$	$\lambda$	$\nu$	$\Delta\nu$
703·90	142065·6		508·23	196761·3	
		204·2			186·0
702·89	142269·8		507·75	196947·3	
		107·3			116·4
702·36	142377·1		507·45	197063·7	

The means of the separations are 195 and 112, as compared with 179 and 136 for the three lines under consideration. The discordance is larger than would be expected if the separations are really identical, as it is estimated that the wave-length separations may be relied upon to about 0·01 Å ('Phil. Mag.,' vol. 48, p. 259, 1924). It does not seem possible to reach a final decision, however, until the measurements have been checked, or the structure of the O III spectrum has been more fully investigated.]

As no intercombinations between the doublet and quartet systems have been identified, the tabulated terms of the quartet system are entirely based upon an assumed value of 100,000 for the  $a^4p_3$  term. It will be understood that while the stated values of the terms themselves may be grossly in error, their differences are exact within the limits of error of the observations.

#### THE DOUBLET SYSTEM.

The terms of the doublet system which have so far been traced are collected in Table II, it being understood that the values stated have been reached on the supposition that three of the  $p$  terms form an ordinary sequence, having  $4^1R$  for the series constant. The adopted values of some of the terms have been derived from measurements of a high order of accuracy ; otherwise, the values

are the means of the determinations from the various combinations into which they enter. The general accuracy of the measurements throughout is indicated by the close agreement between the observed wave-numbers of the lines and those obtained from differences of the corresponding terms.

Table II.—Terms of the Doublet System.

1 $s_1$	[238,816]*		$as'_1$	87310.5	
2 $s_1$	79078.69		$bs'_1$	27398.5	
		$\Delta\nu$			
2 $p_1$	94132.52	179.99	$ap'_1$	68851.16	$\Delta\nu$
2 $p_2$	93952.53		$ap'_2$	68791.42	59.74
3 $p_1$	42692.15	187.53	$bp'_1$	50540.8	
3 $p_2$	42504.62		$bp'_2$	50494.2	46.6
4 $p_1$	24612.3				
4 $p_2$	24419.2	193.1	$\dagger ad'_2$	76049.6	
			$ad'_2$	76048.6	1.0
$\dagger ap''_2$	49590.80	113.99	$bd'_2$	48618.42	
$ap''_1$	49476.81		$bd'_2$	48565.45	51.97
$bp''_1$	29231.39	2.36	$cd'_2$	29974.67	
$bp''_2$	29229.03		$cd'_2$	29972.55	2.12
			$\dagger dd'_2$	23734.7	
$ad_2$	71498.92	190.68	$dd'_2$	23733.9	0.8
$ad_2$	71308.24				
$\dagger bd_2$	53074.3	21.6			
$bd_2$	53052.7				

\* Extrapolated from 2  $s$ .

† Inverted terms; i.e.,  $p_2 > p_1$ , or  $d_2 > d_1$ .

The combinations of doublet terms are shown in Table III.

It should be remarked that lines corresponding to some of the expected combinations fall outside the range of the present observations and consequently do not appear in the tables. There is, however, a notable exception in the combination  $a d - a p''$ , which might have been expected to appear in the blue part of the visible spectrum. No trace of this has been found, and its absence may be in some way associated with the fact that the  $a p''$  terms are inverted (i.e.,  $a p_2 > a p_1$ ), suggesting a further restricting condition in the combination of terms. The apparent absence of lines corresponding to other combinations which are theoretically possible may generally be attributed to their feeble intensities, since the smaller terms are involved.

In all cases the terms are arranged in increasing order from left to right, and in decreasing order of magnitude downwards in each group of combinations of terms of similar type.

Wave numbers which are enclosed in brackets have been calculated from the respective terms.

Table III.—Doublet Combinations.

 $^2s\ ^2p$  Combinations.

$2s_1 = 79078.69$

 $\Delta\nu$ .

$2p_2 = 2s_1 = 14873.87(5)$	$180.18$	$2p_2 = 93952.53$
$2p_1 = 2s_1 = 15054.05(4)$		$2p_1 = 94132.52$
$2s_1 = 3p_1 = 36386.52(6)$	$187.95$	$3p_1 = 42692.15$
$2s_1 = 3p_2 = 36574.47(10)$		$3p_2 = 42504.62$
$2s_1 = ap'_2 = 29487.92(8)$	$113.94$	$ap'_2 = 49590.80$
$2s_1 = ap'_1 = 29601.86(7)$		$ap'_1 = 49476.81$

 $^2d\ ^2p$  and  $^2d\ ^2p''$  Combinations.

Term Values.	$ad_2$ 71308.24	$190.68$	$ad_1$ 71498.92	Combinations.
$2p_1 = 94132.52$ $179.99$			$22633.60(8)$ $179.98$	$2p - ad$
$2p_2 = 93952.53$	$22644.29(10)$	$190.67$	$22453.62(6)$	
$3p_1 = 42692.15$ $187.53$			$28806.74(5)$ $187.47$	$ad - 3p$
$3p_2 = 42504.62$	$28803.50(8)$	$190.71$	$28994.21(5)$	
$4p_1 = 24612.3$ $193.1$			$*46888.3(5)$	$ad - 4p$
$4p_2 = 24419.2$	$*46888.3(5)$		$47079.7(1)$	
$bp'_1 = 29231.39$ $2.36$			$42267.7(3)$ $2.2$	$ad - bp''$
$bp'_2 = 29229.03$	$42079.5(4)$	$190.4$	$42269.9(1)$	
	$bd_2$ 53052.7	$21.6$	$bd_1$ 53074.3	
$2p_1 = 94132.52$ $179.99$	$41079.6(9)$ $179.8$			$2p - bd$
$2p_2 = 93952.53$	$40899.8(5)$	$21.6$	$40878.2(10)$	
$bp'_1 = 29231.39$ $2.36$	$23821.44(1)$ $[2.4]$			$bd - bp''$
$bp'_2 = 29229.03$	$[23823.8]$	$[21.6]$	$23845.42(2)$	

\* Not resolved.

 $^2s'\ ^2p'$  Combinations.

$as'_1 = 87310.5$

$bs'_1 = 27398.5$

$as'_1 - bp'_1 = 36769.5(2)$

$bp'_1 = 50540.8$

$as'_1 - bp'_2 = 36816.4(3)$

$bp'_2 = 50494.2$

 $46.9$ 

$bp'_2 - bs'_1 = 23095.58(2)$

 $46.46$ 

$bp'_1 - bs'_1 = 23142.04(1)$

$ap'_2 - bs'_1 = 41393.0(3)$

$ap'_2 = 68791.42$

$ap'_1 - bs'_1 = 41452.9(3)$

 $59.9$ 

$ap'_1 = 68651.16$

Table III—continued.

 ${}^2p'{}^2d'$  Combinations.

Term Values.	$ap'_1$ 68791.42	59.74	$ap'_1$ 68851.16	Combinations.
$bd'_2 = 48618.42$ 51.97	20172.84 (3)	59.86	20232.70 (5)	$ap' - bd'$
$bd'_2 = 48565.45$	51.92 20224.76 (7)			
$cd'_2 = 29974.67$ 2.12	38816.65 (1)	59.89	38876.54 (4)	$ap' - cd'$
$cd'_2 = 29972.55$	2.15 38818.80 (6)			
$dd'_2 = 23734.7$ 0.8	45056.8 (2)			$ap' - dd'$
$dd'_2 = 23733.9$	[0.8] [45057.6]	[59.8]	45117.4 (1)	
	$bp'_2$ 50494.2	46.6	$bp'_1$ 50540.8	
$ad'_2 = 76049.6$ 1.0	25555.48 (10)			$ad' - bp'$
$ad'_2 = 76048.6$	0.89 25554.59 (2)	46.89	25507.70 (8)	
$cd'_2 = 29974.67$ 2.12	[20519.44] [2.06]	46.60	20566.04 (3)	$bp' - cd'$
$cd'_2 = 29972.55$	20521.50 (5)			
$dd'_2 = 23734.7$ 0.8	26759.43 (3)			$bp' - dd'$
$dd'_2 = 23733.9$	[0.8] [26760.2]	[46.6]	26806.78 (2)	

 ${}^2p{}^2p'$  and  ${}^2p'{}^2p''$  Combinations.

Term Values.	$ap'_1$ 68791.42	59.74	$ap'_1$ 68851.16	Combinations.
$2p_1 = 94132.52$ 179.99	25341.10 (5)	59.74	25281.36 (7)	$2p - ap'$
$2p_2 = 93952.53$	179.98 25161.12 (10)	59.75	25101.37 (5)	
$3p_1 = 42692.15$ 187.53	26099.22 (4r)	59.88	26159.10 (4r)	$ap' - 3p$
$3p_2 = 42504.62$	187.41 26286.63 (6r)	59.89	26346.52 (3r)	
$4p_1 = 24612.3$ 193.1	44179.3 (1)	59.3	44238.6 (2)	$ap' - 4p^*$
$4p_2 = 24419.2$	194.1 44373.4 (3)	57.2	44430.6 (1)	
$ap''_2 = 49590.80$ 113.99	19200.58 (5)	59.82	19260.40 (3)	$ap' - ap''$
$ap''_1 = 49476.81$	113.99 19314.57 (2)	59.82	19374.39 (4)	
$bp''_1 = 29231.39$ 2.36	39560.2 (1)	59.6	39619.8 (3)	$ap' - bp''$
$bp''_2 = 29229.03$	2.2 39562.4 (4)	59.6	39622.0 (1)	

\* Provisional wave-numbers.

Table III—continued.

 $^2p\ ^2p'$  and  $^2p'\ ^2p''$  Combinations—continued.

	$bp'_1$ 50494.2	46.6	$bp'_1$ 50540.8	Combinations.
$2p_1 = 94132.52$ 179.99	43638.2 (4) 180.0	46.7	43591.5 (6) 179.9	$2p - bp'$
$2p_2 = 93952.53$	43458.2 (8)	46.6	43411.6 (5)	
$bp''_1 = 29231.39$ 2.36	21262.70 (0) 2.40	46.63	21309.33 (1) 2.27	$bp' - bp''$
$bp''_2 = 29229.03$	21265.10 (2)	46.50	21311.60 (0)	

 $^2d\ ^2d'$  Combinations.

Term Values.	$ad_2$ 71308.24	190.68	$ad_2$ 71498.92	Combinations.
$bd'_1 = 48618.42$ 51.97	22689.86 (1) 51.98	190.80	22880.66 (4) 51.96	$ad - bd'$
$bd'_2 = 48565.45$	22741.84 (7)	190.78	22932.62 (1)	
$cd'_2 = 29974.67$ 2.12	41333.7 (1) 2.0	190.7	41524.4 (4) 2.1	$ad - cd'$
$cd'_3 = 29972.55$	41335.7 (6)	190.4	41526.5 (1)	
$dd'_3 = 23734.7$ 0.8	47574.4 (4)	—	—	$ad - dd'$
$dd'_4 = 23733.9$	—	—	47765.3 (2)	
	$bd_2$ 53052.7	21.6	$bd_2$ 53074.3	
$ad'_3 = 76049.6$ 1.0	[22996.9]	—	22975.33 (6)	$ad' - bd$
$ad'_4 = 76048.6$	22995.06 (5)	[21.6]	[22974.3]	
$cd'_2 = 29974.67$ 2.12	23078.15 (2) 2.23	21.32	23099.47 (0) 2.19	$bd - cd'$
$cd'_3 = 29972.55$	23080.38 (0)	21.26	23101.66 (3)	
$dd'_3 = 23734.7$ 0.8	[29318.0]	—	29339.68 (7n)	
$dd'_4 = 23733.9$	29318.50 (6n)	—	[29340.4]	

Attention should also be directed to the following lines of somewhat doubtful classification :—

Term Values.	$ad_2$ 71308.24	190.68	$ad_2$ 71498.92	Combinations.
$xd'_2 = 92582.48$ 48.92	21274.23 (7) 48.92	190.67	21083.56 (3) 48.75	$xd' - ad$
$xd'_3 = 92533.64$	21225.31 (5)	190.50	21034.81 (2)	

Combinations of the quartet terms are indicated in Table V, which is in the same form as Table III.

Table V.—Quartet Combinations.

 $^4s\ ^4p$  Combinations.

$s_2 = 73337.20$

	$\Delta\nu$	
$ap_3 - s_2 = 26662.74$ (9)	158.52	$ap_3 = 100000.00$
$ap_2 - s_2 = 26821.28$ (8)	105.32	$ap_2 = 100158.52$
$ap_1 - s_2 = 26926.58$ (7)		$ap_1 = 100263.84$
$s_2 - bp_1 = 26464.35$ (4r)	105.28	$bp_1 = 46872.88$
$s_2 - bp_2 = 26569.63$ (5r)	161.35	$bp_2 = 46767.66$
$s_2 - bp_3 = 26730.98$ (6r)		$bp_3 = 46606.24$

 $^4d\ ^4p$  and  $^4d\ ^4f$  Combinations.

Term Values.	$d_4$ 78496.68	$d_3$ 78621.30	$d_2$ 78712.86	$d_1$ 78768.40
$ap_1 = 100263.84$ 105.32			21550.98(6) 105.34	55.55 21495.43(6) 105.314
$ap_2 = 100158.52$ 158.52		21537.23(9) 158.53	91.59 21445.64(9) 158.49	55.52 21390.12(4)
$ap_3 = 100000.00$	21503.32(10)	124.62 21378.70(8)	91.55 21287.15(2)	(ap - d)
$bp_1 = 46872.88$ 105.22			31840.27(4r) 105.10	55.37 31895.64(3r) 105.18
$bp_2 = 46767.66$ 161.42		31853.78(8r) 161.36	91.59 31945.37(7r) 161.38	55.45 32000.82(2r)
$bp_3 = 46606.24$	31890.56(10r)	124.58 32015.14(6r)	91.61 32106.75(1r)	(ad - bp)
$f_3 = 54203.15$ 54.03		24418.05(0) 54.15	91.69 24509.74(4) 53.96	55.57 24505.31(4)
$f_2 = 54149.12$ 77.91	24347.57(0) 77.88	124.63 24472.20(3) 77.91	91.50 24563.70(6)	
$f_4 = 54071.21$ 102.27	24425.46(5) 102.29	124.66 24550.11(8)		
$f_5 = 53968.94$	24527.74(10)			(d - f)

 $^4p\ ^4p'$  Combinations.

Term Values.	$p'_3$ 77014.96	$p'_2$ 77106.93	$p'_1$ 77153.03	Combina- tions.
$ap_1 = 100263.84$ 105.32		23156.88 (8) 105.18	46.08 23110.80 (3) 105.30	ap - p'
$ap_2 = 100158.52$ 158.52	23143.55 (8) 158.50	91.85 23051.70 (8) 158.61	46.20 23005.50 (7)	
$ap_3 = 100000.00$	22985.05 (8)	91.96 22893.09 (7)		
$bp_1 = 46872.88$ 105.22		30233.87 (6r) 105.25	46.16 30280.03 (3r) 105.19	p' - bp
$bp_2 = 46767.66$ 161.42	30247.13 (6r) 161.55	91.99 30339.12 (4r) 161.41	46.10 30385.22 (5r)	
$bp_3 = 46606.24$	30408.68 (6r)	91.85 30500.53 (7r)		



Table V—continued.  
 ${}^4d' {}^4p'$  and  ${}^4d' {}^4d$  Combinations.

Term Values.	$d'_4$ 52745.34	6.35	$d'_3$ 52751.69	1.53	$d'_2$ 52753.22	0.47	$d'_1$ 52753.69
$p'_1 = 77153.03$ 46.10					24399.76 (4) 46.08	0.42	24399.34 (1)
$p'_2 = 77106.93$ 91.97			24355.24 (5) 91.99	1.56	24353.68 (7) 91.90		[24353.26]
$p'_3 = 77014.96$	24269.61 (8)	6.36	24263.25 (3)	1.47	24261.78 (2)		( $p' - d'$ )
$d_1 = 78768.40$ 55.54					26015.20 (3) 55.51		[26014.71]
$d_2 = 78712.86$ 91.56			25961.22 (2) 91.63	1.53	25959.69 (3) 91.63		[25959.17]
$d_3 = 78621.30$ 124.62	25875.96 (2) 124.59	6.37	25869.59 (5) 124.57	1.53	25868.06 (1)		
$d_4 = 78496.68$	25751.37 (7)	6.35	25745.02 (3)				

$x {}^4d$ ,  $x {}^4p'$  and  $x {}^4s$  Combinations.

$$x_3 = 52702.93$$

	$\Delta\nu$	
$d_4 - x_3 = 25793.70$ (4)	124.65	$d_4 = 78496.68$
$d_3 - x_3 = 25918.35$ (4)	91.70	$d_3 = 78621.30$
$d_2 - x_3 = 26010.05$ (3)		$d_2 = 78712.86$
$p'_3 - x_3 = 24312.00$ (4)	91.98	$p'_3 = 77014.96$
$p'_2 - x_3 = 24403.98$ (3)		$p'_2 = 77106.93$
$s_2 - x_3 = 20634.04$ (1)		$s_1 = 73337.26$

The value of  $j_x$  which satisfies the above combinations is clearly 3, but the character of the  $x$  term remains uncertain; it may be an unresolved  ${}^4p$  or  ${}^4d'$  term, or possibly a term of the sextet system.

The combination  ${}^4s {}^4d'$  also occurs, as will appear from the following:

Calculated	Observed.
$s_2 - d'_1 = 20583.57$	20583.88 (3)
$s_2 - d'_2 = 20584.03$	
$s_2 - d'_3 = 20585.56$	20585.27 (2)

The following lines involving already recognised  $\Delta\nu$  may also be noted:

23277.34 (3)	23978.50 (4)	91.92
23382.40 (4)	24070.42 (7)	
	24125.84 (2)	55.42

## COMPARISON OF O II AND N I.

The atomic number of oxygen being 8 and that of nitrogen 7, it is to be expected that the spectrum of singly-ionised oxygen (O II) will be of a similar character to that of neutral nitrogen (N I). The lines of O II, however, will be of higher frequencies than corresponding lines of N I in consequence of the greater charge of the "atomic residue," or "core," with respect to the emitting electron, and separations in corresponding pairs or groups may be expected to be larger in O II than in N I.

The spectrum of N I has recently become more completely known through the experiments of Merton and Pilley,\* and a preliminary analysis of the spectrum has been made by C. C. Kiess.† It results that the spectrum is built up from doublet and quartet terms, the largest identified term of each system being of  $p$  type. Although it is not yet possible to make an extensive comparison of the two spectra, it will be of interest to compare some of the probably corresponding terms and combinations. The doublets of N I not yet having been worked out in sufficient detail for effective comparison with O II, attention will be confined to the quartet systems.

Among the quartet combinations which may be compared are the following  $sp$  groups, the notation being that adopted for O II in the present communication.

	O II	N I	O II/N I
$a^4p_3 - ^4s_2$	26662.74 (9)	13385.47 (5)	1.992
$a^4p_2 - ^4s_2$	26821.26 (8)	13432.54 (4)	1.997
$a^4p_1 - ^4s_2$	26926.58 (7)	13466.34 (3)	2.000
	$\Delta ap_{32}$ $\Delta ap_{21}$	$\Delta ap_{32}$ $\Delta ap_{21}$	
	158.52 105.32	47.07 33.80	
Ratio { Observed	4.5 : 3	4.2 : 3	
Calculated	5 : 3	5 : 3	
$^4s_2 - b^4p_1$	26464.35 (4)	13061.73	2.026
$^4s_2 - b^4p_2$	26569.63 (5)	13106.07	2.027
$^4s_2 - b^4p_3$	26730.98 (6)	13176.19	2.029
	$\Delta bp_{32}$ $\Delta bp_{21}$	$\Delta bp_{32}$ $\Delta bp_{21}$	
	161.35 105.28	70.12 44.34	
Ratio { Observed	4.6 : 3	4.7 : 3	
Calculated	5 : 3	5 : 3	

\* 'Roy. Soc. Proc.,' A, vol. 107, p. 411 (1925).

† 'Journ. Opt. Soc. America,' vol. 11, p. 1 (1925).

The correspondence for these two triplets is very close. In each spectrum the stronger triplet has the larger separation towards the red, whilst the weaker one has the larger separation towards the violet. In O II the two triplets slightly overlap, whilst in N I they are a little separated. The ratios of the separations are nearly the same in both and approximate to Landé's calculated separations of 5 : 3 for  $4p$  terms. It will also be observed that the wave-numbers in O II are almost exactly double those in N I. The ratios of the separations of the O II to those of the N I triplets, however, are not nearly so constant, being more than 3 : 1 for the first, and about 2·4 : 1 for the second triplet.

Other corresponding quartet combinations, which it is unnecessary to exhibit in full detail, are the following:—

	O II	N I	O II/N I
$a\ ^4p_3 - ^4d_4$	21503·32(10)	11517·11(3)	1·867
$^4d_4 - b^4p_3$	31890·56(10)	15044·84(7)	2·120
	$\Delta d_{43}$ $\Delta d_{32}$ $\Delta d_{21}$	$\Delta d_{43}$ $\Delta d_{32}$ $\Delta d_{21}$	
	124·62 91·56 55·54	50·98 37·35 22·59	
Ratio { Observed	6·81 : 5·00 : 3·03	6·82 : 5·00 : 3·02	
Calculated	7 : 5 : 3	7 : 5 : 3	
$a\ ^4p_3 - ^4p'_3$	22985·05(8)	12167·36(5)	1·889
$^4p'_3 - b^4p_3$	30408·68(9)	14394·51(3)	2·112
	$\Delta p'_{32}$ $\Delta p'_{21}$	$\Delta p'_{32}$ $\Delta p'_{21}$	
	91·97 46·10	38·36 18·38	
Ratio { Observed	6·0 : 3	6·3 : 3	
Calculated	5 : 3	5 : 3	

In all these the wave-numbers of the O II are again roughly double those of the corresponding N I combinations, and the term separations are nearly in the same ratios in the two spectra, though in varying discordance with Landé's rules. The ratios of the term separations of O II to those of N I range from 2·4 to 2·5, and are not very different from those in the second  $sp$  triplet mentioned above.

Only one  $^4d\ ^4f$  multiplet has been identified in each spectrum, namely:—

	O II	N I	O II/N I
$^4d_4 - ^4f_2$	24527·74(10)	15421·32(9)	1·59
	$\Delta f_{54}$ $\Delta f_{43}$ $\Delta f_{32}$	$\Delta f_{54}$ $\Delta f_{43}$ $\Delta f_{32}$	
	102·27 77·91 54·03	56·06 34·70 17·74	
Ratio { Observed	9·19 : 7·00 : 4·85	11·31 : 7·00 : 3·58	
Calculated	9 : 7 : 5	9 : 7 : 5	

In these combinations the wave-number of the leading line of the O II group is much less than double that of the corresponding N I line. Further, although in O II the separation ratios are in close accordance with Landé's rule, those of the N I group are more nearly in the relation 3 : 2 : 1 than 9 : 7 : 5. The total separations,  $\Delta f_{52}$ , however, are in the ratio 2·2 : 1, and in this respect approximate to the ratios of most of the other term separations.

The outcome of the comparison is to suggest a close similarity between the spectra of O II and N I, most of the quartet groups of lines in O II having wave-numbers which are approximately double those of corresponding groups in N I. Apart from the  $a^4p$  and  $4f$  terms, the ratios of the corresponding term separations in O II and N I are nearly constant, and not far from 2·4 : 1.

#### *Summary.*

The spectrum of oxygen in the region  $\lambda$  6750– $\lambda$  1850 has been investigated under different conditions, and many previously unrecorded lines have been measured. In the present communication, particulars are given of about 400 lines, which are attributed to the singly-ionised atom (O II). The structure of this spectrum has been further elucidated, 90 lines having been assigned to the doublet system and 68 to the quartet system.

On the supposition that three of the doublet  $p$  terms form a Rydberg sequence, with 4 R for the series constant, the value 93952 has been assigned to the term  $2^2p_2$ , and the values of other terms have been deduced from the various combinations. The term  $2s$  thus derived suggests about 240,000 for the  $1s$  term, and if this represents the deepest energy level, the corresponding value for the ionisation potential will be about 30 volts, in fair accordance with the 31 volts deduced from stellar spectra. As the calculated  $1s - 2p$  lines lie in the extreme ultra-violet, and have not yet been identified, this result cannot be regarded as final.

As no intercombinations between the doublets and quartets have been traced, the tabulated quartet terms depend upon an arbitrary value assigned to one of them.

So far as a comparison can at present be made, the spectra of O II and N I, as expected, show a close similarity, the wave-numbers of several of the groups of lines in O II being approximately double those of the corresponding groups of N I.

The author has pleasure in acknowledging the effective help which has been given by Mr. E. W. H. Selwyn, B.Sc., in connection with the experimental work which forms the basis of the foregoing paper.

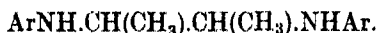
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*Stereoisomeric Diaryl-β-γ-Diamino-N-Butanes.*

By GILBERT T. MORGAN, F.R.S., WILFRED JOHN HICKINBOTTOM and THOMAS  
VIPOND BARKER.

(Received November 17, 1925.)

When condensed with primary aromatic amines, β : γ-dibromobutane or the corresponding dichloride gives rise to secondary diamines of the following type :—

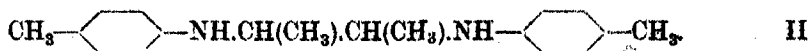


These bases contain two asymmetric carbon atoms, which are either mirror images of each other or absolutely identical. Like the tartaric acids they should therefore exist in an internally-compensated *meso*-form, as well as an externally compensated mixture, potentially resolvable into optically active modifications. Moreover, the externally compensated mixture may belong to one of three categories, being either (1) a true racemoid, inseparable by purely physical agencies ; (2) a conglomerate of *d*- and *l*-crystals, mechanically separable in various ways ; or (3) a pseudo-racemoid, *i.e.*, a special kind of mixed crystal containing *d*- and *l*-material in variable proportions.

The criteria to be applied in the elucidation of any *dl*-mixture are partly crystallographic. A true racemoid generally shows no physical resemblance to its optically active components. But the morphological distinctions between a conglomerate and a pseudo-racemoid are not so sure, for a mixed crystal may be extremely similar to its individual components. Such uncertainties led Roozeboom to advance criteria of a different order, depending on a study of the conditions of equilibrium between the solid and its liquid (or dissolved) phases.

The present investigations bring a highly satisfactory confirmation of the requirements of stereochemical theory, inasmuch as a *meso*-isomeride has been isolated in every case examined. They also furnish an interesting suite of externally compensated mixtures, including, as they do, at least one example of each of the three possible categories.

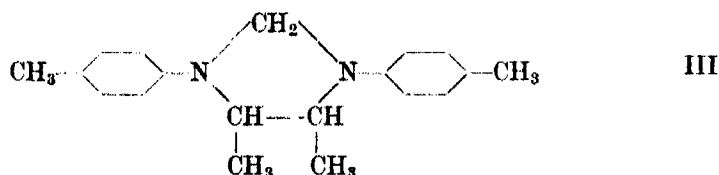
The most fully investigated series of compounds are those in which the *p*-tolyl residue,  $\text{CH}_3\text{.C}_6\text{H}_4$  ... , represents the aryl group of the above general formula. The parent substance, di-*p*-tolyl-β-γ-diamino-*n*-butane (II), has already been described briefly (' Chem. Soc. Trans.,' 1923, vol. 123, p. 97).



A more detailed chemical and crystallographic study has now been made, and its *cyclomethylene*- and *piperazine*-derivatives investigated.

*dl*-Di-*p*-tolyl- $\beta$ - $\gamma$ -diamino-*n*-butane (m.p.  $60^\circ$ ), when crystallised from alcohol or petroleum between  $-15^\circ$  and  $+30^\circ$ , separates as a conglomerate of the *d*- and *l*-modifications. This crystalline condition of the externally compensated diamine has been proved by hand-picking of the enantiomers, and by Gernez's method of inoculating its supersaturated solutions alternately with fragments of the *d*- and *l*-modifications. Moreover, since these diamines have definite melting-points a new method has been applied which is independent of polarimetric or crystallographic observations. From the well-crystallised conglomerate a large separate crystal is selected as a standard. This specimen will consist of one enantiomer (m.p.  $87-88^\circ$ ). A mixed melting-point taken with fragments of this crystal and any other will remain at  $87-88^\circ$  if the two crystals are of the same *d*- or *l*-modification, but will be depressed to  $60^\circ$  approximately if the second crystal is of the other enantiomer. By pursuing this melting-point method any given quantity of crystalline *dl*-conglomerate can be sorted out into two sets of crystals which, after one crystallisation, give the maximum rotation ( $[\alpha]_D \pm 99^\circ$ ) of the purified enantiomers.

The foregoing stereoisomeric di-*p*-tolyl- $\beta$ - $\gamma$ -diamino-*n*-butanes readily react

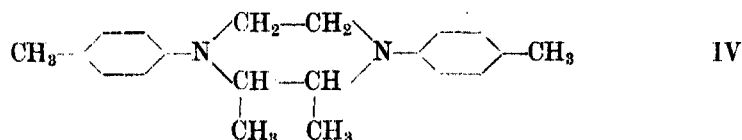


with formaldehyde to give rise to four *cyclomethylenedi-p-tolyl- $\beta$ - $\gamma$ -diamino-*n*-butanes* (III), having the following physical constants :—

	m.p.	$[M]_D$ .
<i>dl</i> -cycloMethylenedi- <i>p</i> -tolyl- $\beta$ - $\gamma$ -diamino- <i>n</i> -butane ..	$107^\circ$ .	
<i>d</i> -cycloMethylenedi- <i>p</i> -tolyl- $\beta$ - $\gamma$ -diamino- <i>n</i> -butane ..	$65-66^\circ - 9.2^\circ$ .	
<i>l</i> -cycloMethylenedi- <i>p</i> -tolyl- $\beta$ - $\gamma$ -diamino- <i>n</i> -butane ..	$65-66^\circ + 11.2^\circ$ .	
<i>meso</i> -cycloMethylenedi- <i>p</i> -tolyl- $\beta$ - $\gamma$ -diamino- <i>n</i> -butane ..	$94^\circ$ .	

Although produced from a secondary *dl*-diamine, which crystallises as a conglomerate of its enantiomers, the *r*-cyclomethylenedi-*p*-tolyl- $\beta$ - $\gamma$ -diamino-*n*-butane is a true racemoid compound. It crystallises in monoclinic prisms, which show no resemblance to the crystals of the *d*- or *l*-modification. The failure to effect any separation by the methods of hand-picking, inoculation and mixed melting-points also point to this conclusion.

The stereoisomeric di-*p*-tolyl- $\beta$ - $\gamma$ -diamino-*n*-butanes condense with ethylene



dibromide in presence of alkali to furnish the corresponding 1 : 4-*di-p*-tolyl-2 : 3-dimethylpiperazines (IV) having the following physical constants :—

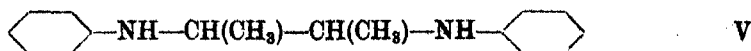
	m.p.	[M] <sub>D</sub>
<i>dl</i> -1 : 4-Di- <i>p</i> -tolyl-2 : 3-dimethylpiperazine	.. 110-111°.	
<i>d</i> -1 : 4-Di- <i>p</i> -tolyl-2 : 3-dimethylpiperazine	.. 138·5°	—116·1°.
<i>l</i> -1 : 4-Di- <i>p</i> -tolyl-2 : 3-dimethylpiperazine	.. 138·5°	+114·4°.
<i>meso</i> -1 : 4-Di- <i>p</i> -tolyl-2 : 3-dimethylpiperazine	.. 83-84°.	

The *dl*-mixture crystallises in a form which is extremely similar to that of the *d*-rotatory component, the possibility of its being a true racemoid being thereby excluded. As indicated previously, any further distinction between a conglomerate and a pseudo-racemoid presupposes evidence of another kind. This has been obtained by studying the melting-point curves of various mixtures of the two enantiomers (prepared by adding the *d*-rotatory component to the *dl*-mixture), the conclusions being that we have here to deal with a pseudo-racemoid.

Owing, however, to the difficulty of determining the melting-points with precision, the most decisive results were obtained by applying the hand-picking method; determining the melting-point of each individual crystal separated from solutions of *dl*, *d* and *l* forms. This method supplies a new criterion of the pseudo-racemoid nature of a *dl* substance (see p. 515).

The syntheses of di-*p*-tolyl- $\beta$  :  $\gamma$ -diamino-*n*-butane and its cyclomethylene and piperazine derivatives have accordingly furnished examples of the three possible categories of *dl*-mixtures, namely, conglomerate, racemoid and pseudo-racemoid respectively.

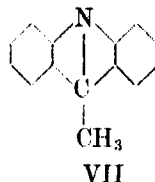
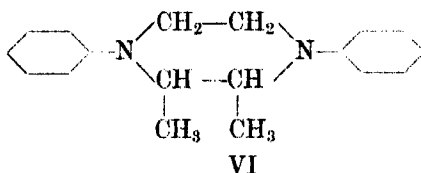
When *p*-toluidine is replaced by aniline in the condensation with  $\beta$ - $\gamma$ -dibromobutane, the diphenyl- $\beta$ - $\gamma$ -diaminobutanes (V) are produced.



In this case the *dl*- and *meso*-diamines are uncrystallisable oils. The former was, however, identified by conversion into the corresponding piperazine (VI), which was then resolved into its enantiomers. A study of the physical properties

of the *dl*-piperazine and its *d*-rotatory component leads to the conclusion that the former is a true racemoid. The balance of the crystallographic evidence points the same way, although it is not so conclusive as usual.

In the reaction between aniline and  $\beta$ - $\gamma$ -dibromobutane the yield of *meso*-diamine (V) is very small, although this stereoisomeride is always formed under the experimental conditions giving rise to the *dl*-variety.



At higher temperatures and in the presence of excess of aniline, 5-methylacridine (VII) is produced in small yield.

#### EXPERIMENTAL.

##### I. Stereoisomeric Di-*p*-tolyl- $\beta$ - $\gamma$ -diamino-n-butanes.

*p*-Toluidine reacts more readily with  $\beta$ - $\gamma$ -dibromobutane than with the corresponding dichloro-compound, and accordingly the conditions formerly described for the preparation of di-*p*-tolyl- $\beta$ - $\gamma$ -di-*n*-butanes (*loc. cit.*) have been modified as follows, in order to obtain a satisfactory yield of the stereoisomeric diamines without the formation of 3 : 5 : 7-trimethylacridine as a by-product.

Commercially pure *p*-toluidine (100 grams) and 50 grams of purified  $\beta$ - $\gamma$ -dibromobutane (b.p. 157-158°) were heated at 105-110° for 35-36 hours the temperature being finally raised to 150-160° for one hour. After adding aqueous sodium carbonate to the mixture, excess of *p*-toluidine was removed by distillation in steam, the diamines were extracted from the residue with benzene and converted into their hydrochlorides by shaking this extract with 70 c.c. of concentrated hydrochloric acid and 200 c.c. of water. When cooled overnight, the crystalline mass of crude hydrochlorides was washed with small amounts of hydrochloric acid.

The mixed hydrochlorides were decomposed with ammonia, the diamines extracted with benzene, and this extract, after washing and drying, was warmed with 20 grams of dry powdered picric acid, when the crystalline *dl*-di-*p*-tolyl- $\beta$ - $\gamma$ -diamino-*n*-butane picrate which separated was washed with benzene and ether.

The filtrates and mother liquors were rendered ammoniacal, the benzene-ether extract of the diamines was separated, washed, dried and distilled to



remove solvents. The residual oily bases were converted into hydrochlorides by adding alcoholic hydrochloric acid, and after drying, the crude salt was extracted with absolute alcohol, leaving a residue of pure *meso*-di-*p*-tolyl- $\beta$ - $\gamma$ -diamino-*n*-butane hydrochloride. The alcoholic filtrates from the *meso*-salt were concentrated and poured into chloroform. when the crystalline precipitate of mixed hydrochlorides thus obtained was worked up by a repetition of the picrate separation.

The yields of *dl*- and *meso*-diamines were respectively 36 and 12 per cent. of the calculated quantity reckoned on the weight of  $\beta$ - $\gamma$ -dibromobutane employed.

*The Crystalline Condition of dl-di-p-tolyl- $\beta$ - $\gamma$ -diamino-n-butane.*—The *dl*-diamine was resolved by means of *d*- $\alpha$ -bromocamphor- $\pi$ -sulphonic acid into its *d* and *l* components, and a preliminary examination of the crystals (*loc. cit.*) showed that the *dl* form is almost identical crystallographically with the active enantiomers. This identity may be due either to spontaneous resolution into an optically active conglomerate or to the occurrence of the *dl* form in a pseudo-racemoid condition. This question has now been decided by a detailed study of the *dl* form and its active components.

*Melting-Points of Mixtures of d- and l-di-p-tolyl- $\beta$ - $\gamma$ -diamino-n-butan.*—Accurate determinations of the temperature of fusion for mixtures containing approximately 50 per cent. of each component were of considerable importance in deciding the shape of the melting-point curve, and known weights of one of the active diamines were added to weighed amounts of the *dl* base. These mixtures were fused, allowed to solidify in the desiccator, and small portions of the powdered solid warmed in thin-walled tubes attached to thermometer (graduated in  $0.1^\circ$ ) until the last trace of solid had disappeared, this temperature being taken as the melting-point of the mixture. Concordant results were obtained when the mixture contained in each melting-point tube was fused and allowed to resolidify before the melting-point was taken. In fig. 1 the observed melting-points are plotted against the composition of each mixture.

These experiments show that *dl*-di-*p*-tolyl- $\beta$ - $\gamma$ -diamino-*n*-butane crystallises as a conglomerate of optically active enantiomers.

*Separation of dl-di-p-tolyl- $\beta$ - $\gamma$ -diamino-n-butane into Optically Active Components.*—The new procedure described below is applicable to all conglomerates having a definite melting-point and is not dependent on an examination of the hemihedrism of the crystals. This method is based on the following considerations :—

- (a) When an externally compensated substance is deposited from solution as a conglomerate, each separate crystal consists of one of the pure optically active components.
- (b) The melting-point of each crystal is depressed by admixture with its enantiomorph.

The largest individual crystal melting at  $86^\circ$  was selected from a crop of the crystallised *dl*-diamine and used as a standard of reference. The melting-point of a portion of any other separate crystal was determined first alone and when mixed with an equal amount of the standard crystal. The crystals thus examined were sorted into two heaps; one set where the melting-point

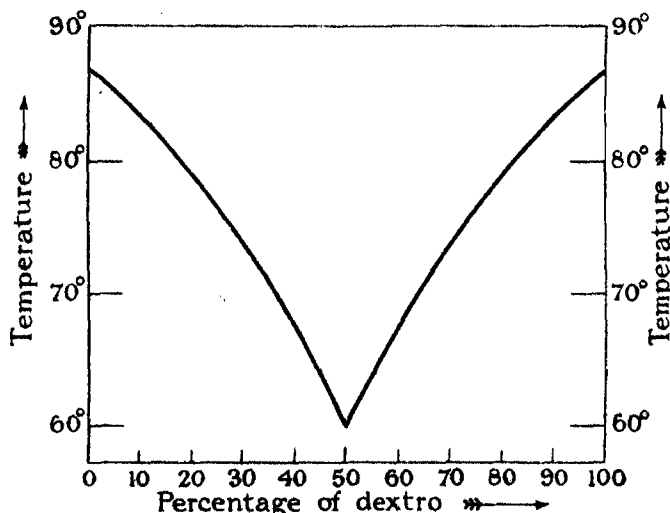


Fig. 1.

remained unchanged on mixing with the standard crystal, thus indicating crystalline identity with the standard specimen; the other set where the melting-point was depressed to  $60^\circ$ , thus revealing the enantiomorphous condition.

In one of these separations the rotatory powers of the two groups of separated crystals were respectively  $[\alpha]_D + 89^\circ$  and  $-76^\circ$  (the maximum value being  $\pm 99^\circ$ ). One crystallisation from alcohol sufficed in each case to yield products with the maximum rotation.

The *dl*-base was crystallised both from alcohol and petroleum (b.p.  $40$ - $60^\circ$ ) over a temperature range of  $-15^\circ$  to  $+30^\circ$ . Each crop was separated by the melting-point method into *d* and *l* forms, and no evidence of the presence of a racemoid compound could be detected within these limits of temperature.

*Resolution of dl-Di-p-tolyl- $\beta$ - $\gamma$ -diamino-n-butane by inoculating its Solutions alternatively with d- and l-amines.*—It was shown by Gernez ('Compt. Rend.,' 1866, vol. 63, p. 843) that a supersaturated solution of an externally compensated substance, which exists as a conglomerate at the temperature of the experiment, when inoculated with a fragment of one of its components deposits the excess of solute as the component having the same sign of rotation as the inoculating crystal. This observation was utilised by Purdie ('J. Chem. Soc.,' 1893, vol. 63, p. 1143) in resolving *dl*-zinc ammonium lactate.

This method can be applied to the resolution of *dl*-di-*p*-tolyl- $\beta$ - $\gamma$ -diamino-*n*-butane, providing that the temperature is constant and that the solutions are not too highly concentrated. It was found necessary also to exclude atmospheric dust, the particles of which might serve as nuclei for the deposition of both forms.

A slightly supersaturated alcoholic solution of the externally compensated diamine was heated to boiling in large, loosely stoppered weighing-bottles, which had been previously steamed and dried. The condensed solvent ran back down the walls of the bottles dissolving completely any traces of solid *dl* base. After cooling the solutions in a desiccator they were inoculated with a minute amount of finely powdered dextrorotatory diamine. The crystals which separated were found to be practically pure *d*-di-*p*-tolyl- $\beta$ - $\gamma$ -diamino-*n*-butane. The mother liquors replaced in the weighing-bottles and heated again to boiling were, after cooling, seeded with powdered fragments of the levorotatory diamine. The crystalline deposit consisted of practically pure *l*-di-*p*-tolyl- $\beta$ - $\gamma$ -diamino-*n*-butane. By repeating this process of alternate inoculation with *d*- and *l*-enantiomers, a considerable proportion of the original inactive *dl*-diamine was resolved into its optically active components. Highly concentrated solutions gave deposits of the optically inactive *dl*-diamine, but employing more dilute solutions it was found possible to pass from the inactive base produced by synthesis to the active diamines without direct reference to the asymmetric nature of the crystal.

*The Crystallography of the Stereoisomeric Di-p-tolyl- $\beta$ - $\gamma$ -diamino-n-butan.*—The *d*- and *l*-modifications of this substance crystallise in the orthorhombic system, and are distinguishable from each other by a hemihedral development. The crystals are generally elongated along the vertical axis and tabular parallel to *b* (010), as shown in fig. 2, the forms common to both modifications being *a* (100), *m* (110), *n* (120), *b* (010), and *r* (101). The characteristic hemihedral facets of the *d*-crystals belong to the form *x* (121), but a second hemihedral form (111) is sometimes developed. In the *l*-modification the converse forms

( $\bar{1}\bar{1}1$ ) and  $1\bar{2}1$ ) make their appearance. The axial ratios,  $a : b : c = 0.3531 : 1 : 0.2710$ , were computed from the following results of measurement of five crystals.

	$m$ (110)	$n$ (120)	$r$ (101)	$o$ (111)	$x$ (121)
$\phi$ ..	*70° 34' (-1)	*45° 54' (2)	*90° 1'	70° 49'	54° 58'
$\rho$ ..	90 0	90 0	*37 27	39 0 (5)	43 9 (1)

Twins, with the normal to  $r$  as the twin axis, are not infrequent. The double refraction is strong and positive; the acute bisectrix is normal to  $b$  and the axial plane is  $c$  (001) (with wide angle).

As stated previously, the inactive *dl*-mixture does not form a racemoid compound but separates as a conglomerate of *d*- and *l*- individuals, which are mechanically separable by virtue of their hemihedral development.

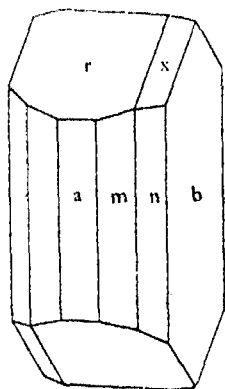


Fig. 2.

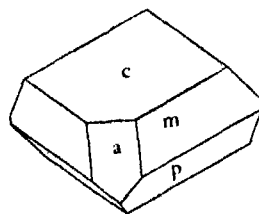


Fig. 3.

The *meso*-isomeride naturally shows no trace of hemihedrism. The system is monoclinic with  $a : b : c = 1.498 : 1 : 1.049$ ,  $\beta = 103^\circ 23'$ . The habit is tabular parallel to  $c$  (001), the other forms being  $m$  (110),  $a$  (100) and  $p$  ( $\bar{1}11$ ), as shown in fig. 3. Following are the results of measurements of four crystals.

	$m$ (110)	$a$ (100)	$c$ (001)	$p$ ( $\bar{1}11$ )
$\phi$ ..	*34° 28'	90° 0'	89° 50' (10)	*335° 19'
$\rho$ ..	90 0	90 0	13 31 (-8)	*49 6

The optic axes lie in the plane of symmetry, one being visible through  $c$ .

## II. Stereoisomeric cycloMethylenedi-*p*-tolyl- $\beta$ - $\gamma$ -diamino-*n*-butanes.

Formaldehyde condenses with the *dl*- and *meso*-forms of di-*p*-tolyl- $\beta$ - $\gamma$ -diamino-*n*-butane in alcoholic solutions to yield well-defined cyclic anhydro-bases having the graphic formula shown on page 503.

Racemic cycloMethylenedi-p-tolyl- $\beta$ - $\gamma$ -diamino-n-butane melts at  $107^\circ$  and its *meso*-isomeride at  $94^\circ$  (*loc. cit.*).

d-cycloMethylenedi-p-tolyl- $\beta$ - $\gamma$ -diamino-n-butane was similarly prepared from the dextro-diamine. The condensation proceeded too rapidly for any accurate polarimetric estimation of the velocity of the reaction. A solution of the *d*-diamine in absolute alcohol ( $\alpha_D + 3.82^\circ$  in 2 dm. tube;  $c = 2.01$ ), when mixed with 1 c.c. of 40 per cent. aqueous formaldehyde, showed a rapid diminution of rotation, reaching  $\alpha_D - 0.07^\circ$  in twenty minutes and  $-0.10^\circ$  in one hour. After twelve hours there was no perceptible rotation. When crystallised from methyl alcohol this cyclomethylene base from the dextro-diamine melted at  $65-66^\circ$ . (Found N = 10.2.  $C_{19}H_{24}N_2$  requires N = 10 per cent.) The substance was sparingly soluble in methyl or ethyl alcohol but dissolved readily in benzene or petroleum. A solution in absolute alcohol had a small *laevo*-rotation ( $\alpha_D - 0.14^\circ$ ,  $c = 2.2$ ,  $l = 2$  [ $\alpha$ ] $_D = -3.3^\circ$ ). Owing to this feeble activity the value of the specific rotation is only approximate.

l-cycloMethylenedi-p-tolyl- $\beta$ - $\gamma$ -diamino-n-butane, prepared in a similar manner from the *laevo*-diamine, melted at  $65-66^\circ$  and had [ $\alpha$ ] $_D + 4^\circ$  approximately. (Found N = 10.17.  $C_{19}H_{24}N_2$  requires N = 10 per cent.)

*Stereoisomeric cycloMethylenedi-p-tolyl- $\beta$ - $\gamma$ -diamino-n-butan*es.—The racemoid modification of this substance crystallises in the monoclinic system with the forms *m* (110), *b* (010), *o* (111), *q* (011) and *c* (001), as shown in fig. 4. The axial ratios  $a : b : c = 1.026 : 1 : 1.300$ ,  $\beta = 102^\circ 43'$  were calculated from the following results of measurement of three crystals:—

	<i>m</i> (110)	<i>c</i> (001)	<i>q</i> (011)	<i>o</i> (111)
$\phi$ .....	$*44^\circ 59'$	$90^\circ 0'$	$*9^\circ 51'$	$49^\circ 29' (4)$
$\rho$ .....	90 0	$*12$ 13	53 2 (—12)	63 36 (—7)

The *d*-modification also crystallises in the monoclinic system, but shows no resemblance to the foregoing. An idealised crystal is shown in fig. 5, the forms being *m* (110), *c* (001), *R* ( $\bar{1}01$ ), *p* ( $\bar{1}11$ ) and rarely *a* (100). There is no sign of any hemihedral development although the structure must be of an enantiomorphous nature. The axial ratios,  $a : b : c = 0.7075 : 1 : 0.8646$ ,  $\beta = 102^\circ 59'$ , were computed from the following results of measurement of three crystals:—

	<i>m</i> (110)	<i>a</i> (100)	<i>c</i> (001)	<i>R</i> ( $\bar{1}01$ )	<i>p</i> ( $\bar{1}11$ )
$\phi$ ..	$*55^\circ 25'$	$90^\circ 0'$	$91^\circ 34'$	$270^\circ 7'$	$310^\circ 26' (-15)$
$\rho$ ..	90 0	90 0	$*12$ 59	$*45$ 40	53 29 (—14)

Double refraction, extremely strong. Extinction on  $m = 16^\circ$  with vertical edge.

The *meso*-isomeride also crystallises in the monoclinic system but shows no resemblance to either of the foregoing. The crystals are tabular parallel to  $b$  (010) as shown in fig. 6, the other forms being  $x$  (021),  $o$  (111),  $m$  (110); and also, rarely,  $n$  (120) and  $a$  (100), not shown in the figure. The constants,

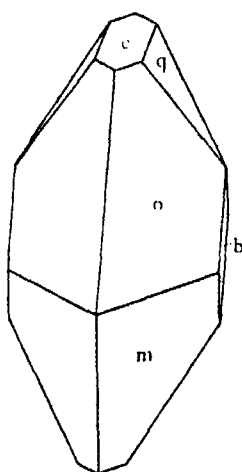


Fig. 4.

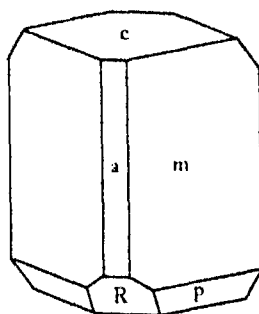


Fig. 5.

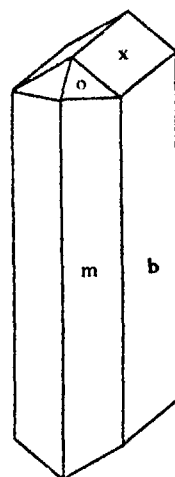


Fig. 6.

$a : b : c = 0.3092 : 1 : 0.2848$ ,  $\beta = 96^\circ 23'$ , were computed from the following results of measurement of three crystals :—

	$m$ (110)	$n$ (120)	$o$ (111)	$x$ (021)
$\phi$ .....	$*72^\circ 55'$	$58^\circ 30' (-5)$	$*74^\circ 40'$	$10^\circ 48' (19)$
$\rho$ .....	90 0	90 0	$*47$ 7	30 10 $(-2)$

There is a good  $b$ -cleavage, normal to which is the positive acute bisectrix. The axial plane is almost parallel to the edge  $bx$ , and the axial angle is wide.

*The Crystalline Condition of dl-cycloMethylenedi-p-tolyl- $\beta$ - $\gamma$ -diamino-n-butan-2-ol.*—The foregoing crystallographic examination of the *dextro*- and *dl*-forms of *cyclomethylenedi-p-tolyl- $\beta$ - $\gamma$ -diamino-n-butane* showed clearly that the externally compensated substance is a true racemoid compound. This conclusion was confirmed by examining the crystals deposited from a solution in light petroleum of approximately equal amounts of *dl*- and *d*-forms. Each individual crystal melted either at  $102$ – $106^\circ$  (limiting values) or at  $60$ – $65^\circ$ , these melting points being approximately those of the original components of the solution. These components were separated almost completely by continuing the process of crystallisation.

The melting-points of the *cyclomethylene* anhydro-bases from the *d*- and *l*-diamines were depressed to 60° by adding a small amount of the *r*-compound.

### III. Stereoisomeric 1 : 4-*Di-p*-tolyl-2 : 3-dimethylpiperazines (IV).

*dl*-Di-*p*-tolyl- $\beta$ - $\gamma$ -diamino-*n*-butane, anhydrous sodium carbonate (1 mol.) and ethylene dibromide (1 mol.), with sufficient toluene to facilitate the condensation, were warmed with stirring to 105-115° for ten hours, the temperature being finally raised to 130° for one hour. The product was treated with water and the organic bases extracted with benzene. To the dehydrated benzene extract was added the calculated amount of picric acid dissolved in acetone. The yellow *picrate* of *dl*-1 : 4-*di-p*-tolyl-2 : 3-dimethylpiperazine separated and was washed with acetone to remove any *picrate* of the unchanged secondary diamine. The piperazine liberated from the *picrate* by ammonia was crystallised repeatedly from petroleum (b.p. 40-60°) and purified further by reversion into *picrate* and crystallisation of this salt from acetone or ethyl acetate. *dl*-1 : 4-*Di-p*-tolyl-2 : 3-dimethylpiperazine (IV) was ultimately obtained from alcohol or petroleum in colourless transparent tabular crystals, m.p. 110-111°. (Found C = 81.94, H = 8.94; N = 9.76.  $C_{20}H_{26}N_2$  requires C = 81.58, H = 8.90, N = 9.52 per cent.)

The *hydrochloride*, readily soluble in alcohol or chloroform, was crystallised from boiling benzene for analysis. (Found Cl = 19.27.  $C_{20}H_{26}N_2$ , 2HCl requires Cl = 19.31 per cent.)

The *picrate*, separating from ethyl acetate in bright yellow masses of flattened needles or four-sided elongated plates, lost solvent of crystallization at 100°. (Found N = 13.7; loss on drying at 100° = 10.4.  $C_{20}H_{26}N_2$ ,  $2C_6H_3O_7N_3$ ,  $CH_3.CO_2.C_2H_5$  requires N = 13.33,  $CH_3.CO_2.C_2H_5$  = 10.48 per cent. After drying at 110°, N = 15.12;  $C_{20}H_{26}N_2$  = 39.2.  $C_{20}H_{26}N_2$ ,  $2C_6H_3O_7N_3$  requires N = 14.89,  $C_{20}H_{26}N_2$  = 39.10 per cent.) The *picrate*, freed from solvent by heating or exposure, softened and darkened at 200° and decomposed at 203-205°.

Meso-1 : 4-*Di-p*-tolyl-2 : 3-dimethylpiperazine (IV), prepared by the method adopted for the *dl*-compound, separated from alcohol in oblique transparent tablets, m.p. 83-84°. (Found C = 81.88, H = 9.15; N = 9.66.  $C_{20}H_{26}N_2$  requires C = 81.58, H = 8.90, N = 9.52 per cent.)

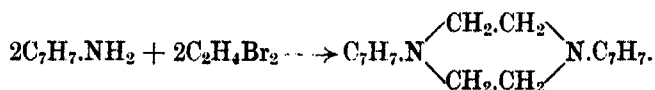
The *hydrochloride*, readily soluble in alcohol or chloroform, separated from ethyl acetate in transparent plates. (Found Cl = 19.15;  $C_{20}H_{26}N_2$ , 2HCl requires Cl = 19.31 per cent.)

The *picrate* crystallised from acetone in bright yellow elongated tablets

melting with decomposition at 194-195°. This preparation contained acetone of crystallisation and lost 11.1 per cent. in weight by heating at 100°. (Found N = 14.99;  $C_{20}H_{26}N_2 = 38.8$ .  $C_{20}H_{26}N_2$ ,  $2C_6H_5O_7N_3$  requires N = 14.89,  $C_{20}H_{26}N_2 = 39.1$  per cent.)

*Observation on the foregoing Piperazine Condensation.*—In condensing *dl*- or *meso*-di-*p*-tolyl-β-γ-diamino-*n*-butane with ethylene dibromide in presence of anhydrous sodium carbonate it was found that on maintaining the temperature at 130-160° for 3 to 8 hours, the basic product of reaction yielded an oil which slowly became semi-solid. The material, which separated in solid form, crystallised from benzene in colourless needles or prisms, m.p. 185-186° (N = 10.87; theory requires N = 10.52 per cent.), and was identified as 1:4-di-*p*-tolylpiperazine. This substance was formed in the condensations whenever the temperature was maintained at 130-160°, although in reactions carried out at 105-115° it was only present in traces. Moreover, its formation is facilitated when the mixture is neither stirred nor diluted with a solvent such as toluene.

It has already been shown that the various forms of di-*p*-tolyl-β-γ-diamino-*n*-butane are decomposed on prolonged heating with acids, and hence the formation of 1:4-di-*p*-tolylpiperazine is most readily explained on the assumption that when local acidity arises through overheating or lack of mixing, some of the diamine is decomposed and the *p*-toluidine liberated reacts with ethylene dibromide in the following sense:—



*Resolution of dl-1:4-Di-p-tolyl-2:3-dimethylpiperazine.*—*d*-α-Bromocamphor-π-sulphonic acid and the *dl*-piperazine yielded only a very soluble gummy product, but Reyhler's *d*-camphorsulphonic acid furnished a crystallisable salt which could be separated into its components, 1:4-Di-*p*-tolyl-2:3-dimethylpiperazine (3.8 grams), dissolved in benzene, was warmed with 5 grams of powdered Reyhler's acid (1.6 mols.) to complete solution. Ethyl acetate was added and the cooled solution inoculated with a fragment of partially resolved camphorsulphonate. The product was crystallised repeatedly from benzene and ethyl acetate when, after three fractionations, the least soluble *d*-camphorsulphonate had  $[\alpha]_D + 28.4^\circ$  ( $c = 5.28$  in alcohol). The separation of a camphorsulphonate of constant rotation was effected only after many more crystallisations. Alternatively the partially resolved camphorsulphonate was decomposed with dilute ammonia and the liberated piperazine crystallised



repeatedly from alcohol. The purified *l*-1 : 4-di-*p*-tolyl-2 : 3-dimethylpiperazine separated from alcohol in colourless leaflets or slowly from petroleum in transparent tablets, m.p. 138.5°. In benzene solution ( $c = 5.66$ )  $[\alpha]_D + 38.9^\circ$ . (Found : C = 81.31 ; H = 9.04 ; N = 9.76.  $C_{20}H_{26}N_2$  requires C = 81.58, H = 8.90, N = 9.52 per cent.)

*d*-1 : 4-Di-*p*-tolyl-2 : 3-dimethylpiperazine.—For the resolution of *dl*-di-*p*-tolyl-dimethylpiperazine into its optically active components only a portion of the externally compensated base was neutralised with camphorsulphonic acid (1.6 mols. instead of 2 mols. for complete neutralisation). Consequently, after the removal of the more sparingly soluble *l*-amine *d*-camphorsulphonate by crystallisation from benzene, there remained in solution a mixture of the free *dextro*-base and its camphorsulphonate.

The optically pure *laevo*-rotatory amine was isolated by taking advantage of the differences of solubility in benzene and in alcohol of the base and its salt. While di-*p*-tolyl-dimethylpiperazine camphorsulphonate was freely soluble in alcohol, sparingly so in benzene, the amine dissolved readily in benzene and with difficulty in cold alcohol.

Accordingly the more soluble fractions from the systematic crystallisation of the camphorsulphonate were freed from benzene and crystallised fractionally from absolute alcohol. *d*-1 : 4-Di-*p*-tolyl-2 : 3-dimethylpiperazine separated and, after further crystallisation from light petroleum, was obtained pure, m.p. 138.5°. In benzene solution ( $c = 4.94$ )  $[\alpha]_D = -39.5^\circ$ . (Found C = 81.84, H = 9.13, N = 9.74.  $C_{20}H_{26}N_2$  requires C = 81.58, H = 8.90, N = 9.52 per cent.)

*Direct Production of Optically Active d*-1 : 4-Di-*p*-tolyl-2 : 3-dimethylpiperazine (V).—Ethylene dibromide, sodium carbonate and *d*-di-*p*-tolyl- $\beta$ - $\gamma$ -diamino-*n*-butane ( $[\alpha]_D + 98^\circ$ ) in molecular proportions were heated together at 110° for 12 to 13 hours as in the preparation of the *dl*-piperazine. The optically active piperazine, isolated through its picrate and crystallised repeatedly from light petroleum (b.p. 40-60°) to free it from traces of di-*p*-tolylpiperazine, was *laevo*rotatory in benzene solution ( $c = 5.57$ ,  $[\alpha]_D - 34.8^\circ$ ), and was finally purified by crystallisation from alcohol,  $[\alpha]_D - 39.5^\circ$ . 1 : 1 : 4-Di-*p*-tolyl-2 : 3-dimethylpiperazine (V), prepared from 1-di-*p*-tolyl- $\beta$ - $\gamma$ -diamino-*n*-butane by the foregoing condensation, was crystallised first from benzene ( $c = 1.13$ ,  $[\alpha]_D + 31^\circ$ ) and then from alcohol when the maximum rotation was obtained,  $[\alpha]_D + 39.5^\circ$ .

The two enantiomers thus prepared by direct condensation were identical in melting-point, 138.5°, and optical activity,  $[\alpha]_D \pm 39.5^\circ$ , with the two

piperazines (p. 514) obtained from the resolution of the externally compensated piperazine.

*The nature of Externally Compensated 1:4-Di-p-tolyl-2:3-dimethylpiperazine.*—The examination of individual crystals of an externally compensated substance usually affords definite evidence of its nature. A racemoid substance yields crystals which are alike in physical properties; from an inactive conglomerate each crystal is optically active and identical with those of the pure components. A pseudo-racemoid product furnishes mixed crystals, which vary continuously in composition between the *d*- and *l*-forms, and consequently individual crystals selected from the synthetic pseudo-racemoid need not be of the same composition.

Such principles are used by crystallographers to discriminate between racemoid substances and conglomerates of *d*- and *l*-forms, but properties other than the external form of the crystals might also be employed. Thus when organic substances are under examination the determination of melting-point of each crystal furnishes evidence of the nature of the externally compensated substance. Moreover, the investigation of such compounds can readily be amplified to confirm earlier results. A solution of a mixture of a racemoid and one of its components deposits crystals which can be separated into active and inactive forms by applying the melting-point method described on pp. 503, 506 and 511. A conglomerate under similar conditions yields a mixture of unequal amounts of *d*- and *l*-antipodes, while a solution of a pseudo-racemoid with one of its components furnishes crystals which should vary in composition.

The behaviour anticipated for individual crystals of pseudo-racemoid substances has been observed with *dl*-1:4-di-*p*-tolyl-2:3-dimethylpiperazine.

A preliminary examination of the form of the fusion curve showed that no depression occurred when the externally compensated amine was mixed with one of its optically active components.

The melting points of the active forms and mixture of 1:4-di-*p*-tolyl-2:3-dimethylpiperazine were determined by heating a small quantity of the powdered substance in a capillary tube attached to a thermometer, the method being similar in its essential features to that employed for di-*p*-tolyl- $\beta$ - $\gamma$ -diamino-*n*-butane. The melting-point recorded is the temperature at which the last trace of solid melted.\*

To decide between a pseudo-racemoid and a conglomerate, the *dl*-base was

\* The general behaviour of these substances is similar to that of *dl*-camphoroxime (Adriani, 'Zeitsch. Physikal. Chem.', 1902, vol. 33, p. 468).

Composition of mixture.		m.p.	Composition of mixture.		m.p.
<i>d.</i>	<i>l.</i>		<i>d.</i>	<i>l.</i>	
100.0	0	140.45	47.4	52.6	13.0
74.6	25.4	127.8	43.7	56.3	117.05
55.1	44.9	114.5	38.7	61.3	120.6
52.4	47.6	112.65	28.6	71.4	127.2
51.0	49.0	111.5	23.4	76.6	131.2
50.0	50.0	111.35	0	100.0	140.85
48.7	51.3	111.7			

crystallised slowly from light petroleum to obtain lustrous well-defined single crystals. The melting point of each crystal was determined in the usual manner by heating some of the powdered substance in a thin-walled capillary tube attached to a thermometer bulb. No sharp melting point was observed. The material became pasty and melted to a clear liquid over a range usually of several degrees. No crystal was isolated having the melting point of the pure active form.

Similar results were obtained when crystals of artificial mixtures of active and inactive forms were crystallised from petroleum (b.p. 80-100°).

It is concluded from these results that externally compensated 1:4-di-*p*-tolyl-2:3-dimethylpiperazine behaves as a pseudo-racemoid substance rather than as a conglomerate.

*d*:1:4-Di-*p*-tolyl-2:3-dimethylpiperazine crystallises in the monoclinic system with  $a : b : c = 3.711 : 1 : 1.894$ ,  $\beta = 115^\circ 13'$ . The habit is tabular parallel to  $a$  (100), as shown in fig. 7, the other forms being  $r$  (101),  $c$  (001),  $R$  ( $\bar{1}01$ ),  $o$  (111) and  $p$  ( $\bar{1}11$ ), and as the two latter forms are holohedrally developed there is no sign of hemihedrism. Following are the results of measurements of two crystals:—

	<i>a</i>	<i>r</i>	<i>c</i>	<i>R</i>	<i>o</i>	<i>p</i>
$\phi$ . . . .	0° 0'	*44° 1'	64° 39' (10)	*95° 18'	44° 4' (-3)	95° 18' (0)
$\rho$ . . . .	90 0	90 0	90 0	90 0	*37 14	27 56 (0)

The optic axes lie in the plane  $b$  (010) and one is visible obliquely through  $a$  (100).

The *dl*-mixture crystallises in forms which are so similar to those of the optically active constituents as to rule out any possibility of it being a true racemoid. The forms actually developed are  $a$  (100),  $c$  (001) and  $o$  (111), and the habit is similar as indicated by fig. 8. The following results of measure-

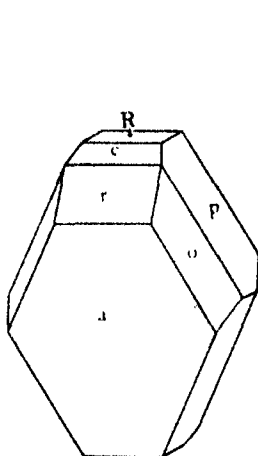


FIG. 7.

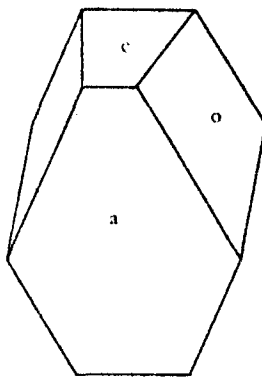


FIG. 8.

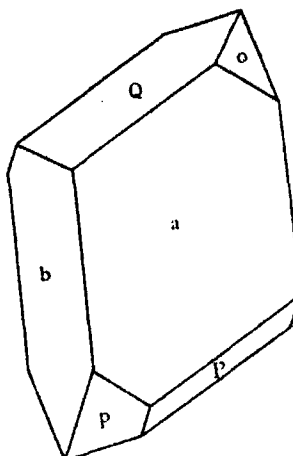


FIG. 9.

ment of four crystals (as also optical properties) afford a general proof of geometrical similarity.

	$a$	$c$	$o$
$\phi$ .....	$0^{\circ} 0'$	$64^{\circ} 36'$	$44^{\circ} 7'$
$\rho$ .....	$90 \quad 0$	$90 \quad 0$	$37 \quad 5$

That the crystals are to be regarded as pseudo-racemoid mixed-crystals, rather than a conglomerate, follows from the evidence derived from a study of melting-points.

The *meso*-isomeride crystallises badly, so that the results of measurement can only be regarded as approximate. The system is anorthic, with  $a : b : c = 0.6814 : 1 : 0.6867$ ,  $\alpha = 95^{\circ} 13'$ ,  $\beta = 92^{\circ} 56'$ ,  $\gamma = 62^{\circ} 5'$ . The habit is shown in fig. 9, the forms being  $a$  (100),  $P$  ( $\bar{1}\bar{1}1$ ),  $p$  ( $\bar{1}1\bar{1}$ ),  $Q$  ( $0\bar{1}\bar{1}$ ) and  $o$  (111). Following are the results of measurement of three crystals:—

	$a$	$P$	$p$	$Q$	$o$
$\phi$ .....	$*117^{\circ} 45'$	$*259^{\circ} 38'$	$*325^{\circ} 20'$	$*175^{\circ} 49'$	$74^{\circ} 0'$
$\rho$ .....	$90 \quad 0$	$*44 \quad 9$	$*59 \quad 20$	$*35 \quad 7$	$48 \quad 1$

#### IV. Diphenyl- $\beta$ - $\gamma$ -diaminobutane.

Aniline (50 gms.) and  $\beta$ - $\gamma$ -dibromobutane (27 gms.) were heated at  $150$ – $160^{\circ}$  for four hours\*; the mixture was then rendered alkaline and distilled in

\* The preparation of diphenyl- $\beta$ - $\gamma$ -diamino-*n*-butane has been described by Trapesonjanz, 'Ber. deutsch. chem. Ges.,' vol. 25, p. 3280 (1892). He concluded that the diamine resulting from the action of dibromobutane on aniline was homogeneous. In reality it was a mixture of *dl*-amine with a small amount of the *meso*-form.

steam to remove excess of aniline. The viscous residue was extracted with benzene; the dried extract after concentration was mixed and stirred with alcohol and dilute nitric acid (20 c.c. of 1.42 acid in 40 c.c. of water). After cooling to  $-10^{\circ}$  the granular nitrate which separated was crystallised fractionally from warm alcohol. The less soluble nitrate was tested by benzylation when benzoyl-*dl*-diphenyl- $\beta$ - $\gamma$ -diamino-*n*-butane was found to be readily soluble in ether, whereas benzoyl-*meso*-diphenyl- $\beta$ - $\gamma$ -diamino-*n*-butane was only very sparingly soluble in this solvent.

*dl*-Diphenyl- $\beta$ - $\gamma$ -diaminobutane (V).—The less soluble nitrate was converted into picrate, and the latter crystallised from alcohol and benzene. The diamine liberated from the purified picrate was a colourless viscous oil, which has not been induced to crystallise. It was miscible in all proportions with the common organic solvents excepting petroleum.

*dl*-Diphenyl- $\beta$ - $\gamma$ -diaminobutane hydrochloride separated from alcoholic hydrochloric acid in white glistening leaflets, m.p.  $205-208^{\circ}$ . (Found Cl = 22.44.  $C_{16}H_{20}N_2$ , 2HCl requires Cl = 22.65 per cent.)

The sulphate\* separated from alcohol in colourless needles. (Found  $H_2SO_4$  = 28.95.  $C_{16}H_{20}N_2$ ,  $H_2SO_4$  requires  $H_2SO_4$  = 28.99 per cent.)

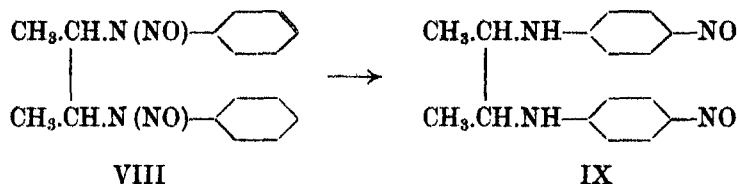
The nitrate, a colourless crystalline powder decomposing at  $170-173^{\circ}$ , was sparingly soluble in cold alcohol. (Found N = 15.34.  $C_{16}H_{20}N_2$ , 2HNO<sub>3</sub> requires N = 15.30 per cent.)

The picrate crystallised from alcohol in rosettes of bronzy red needles with yellow streak, m.p.  $136^{\circ}$ . (Found N = 14.91.  $C_{16}H_{20}N_2$ ,  $C_6H_3O_7N_3$  requires N = 14.91 per cent.) The picrate was readily soluble in acetone or chloroform, but only sparingly so in benzene or ether.

\* 5-Methylacridine (VII) was produced by heating *dl*-diphenyl- $\beta$ - $\gamma$ -diamino-*n*-butane sulphate with excess of aniline at  $200-230^{\circ}$  for 30 hours. After distillation in steam, 5-methyl-acridine was isolated from the residue through its hydrochloride and crystalline yellow tartrate, the latter salt being sparingly soluble in alcohol. When prepared by this condensation 5-methylacridine melted at  $110-112^{\circ}$  (compare Königs, 'Ber.', 1899, vol. 32, p. 3607). The following salts served to characterise the base:—Hydrochloride,  $C_{14}H_{11}N$ , HCl, 2H<sub>2</sub>O, yellow needles sparingly soluble in cold water losing 2H<sub>2</sub>O at  $100^{\circ}$ ; hydrobromide,  $C_{14}H_{11}N$ , HBr, CHCl<sub>3</sub>, from chloroform in yellow acicular prisms losing solvent of crystallisation *in vacuo*; hydroiodide,  $C_{14}H_{11}N$ , HI, H<sub>2</sub>O, yellow needles from water.

The diphenyl- $\beta$ - $\gamma$ -diamino-*n*-butanes, the *p*-tolyl homologues and their nitrated derivatives are decomposed by heating with acids into primary amines, the decomposition proceeding more readily with the nitro-compounds ('J. Soc. Chem. Ind.', 1924, vol. 43, p. 307T) than with the unsubstituted diamines. A similar decomposition is responsible for the foregoing production of 5-methylacridine and for the formation of ditolyl-piperazine (p. 513).

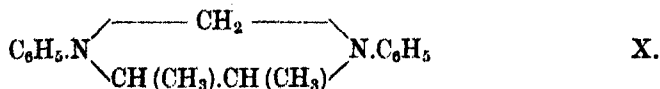
dl-n-Butylene- $\beta$ - $\gamma$ -diphenyldinitrosoamine (VIII).—



On adding sodium nitrite to an acidified solution of the sulphate at  $0^\circ$  the dinitrosoamine was deposited in crystalline form, the precipitation being facilitated by a small amount of ether. Recrystallised from petroleum (b.p.  $80$ – $100^\circ$ ) the dinitrosoamine separated in pale yellowish needles, m.p.  $101^\circ$ . (Found N =  $18.91$ .  $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_4$  requires N =  $18.79$  per cent.)

dl-Di-p-nitrosodiphenyl- $\beta$ - $\gamma$ -diamino-n-butane (IX).—To a warm solution of the preceding dinitrosoamine (1 gm.) in 8 c.c. of glacial acetic acid was added an equal volume of concentrated hydrochloric acid, when dl-di-p-nitrosodiphenyl- $\beta$ - $\gamma$ -diamino-n-butane hydrochloride slowly separated in reddish-brown crystals with a blue metallic lustre. (Found Cl =  $18.95$ .  $\text{C}_{16}\text{H}_{18}\text{O}_2\text{N}_4 \cdot 2\text{HCl}$  requires Cl =  $19.11$  per cent.) The base set free by dilute ammonia or aqueous sodium carbonate crystallised from acetone in dark blue nodules having a brown streak; it melted with decomposition at  $205^\circ$ . (Found N =  $19.11$ .  $\text{C}_{16}\text{H}_{18}\text{O}_2\text{N}_4$  requires N =  $18.79$  per cent.) This dinitroso derivative was sparingly soluble in ether or benzene.

dl-cycloMethylenediphenyl- $\beta$ - $\gamma$ -diamino-n-butane (X).



On adding aqueous formaldehyde to an alcoholic solution of the oily dl-diphenyl- $\beta$ - $\gamma$ -diaminobutane, a solid cyclomethylene base was obtained crystallising in colourless flattened needles, m.p.  $99$ – $100^\circ$ . (Found N =  $11.33$ .  $\text{C}_{17}\text{H}_{20}\text{N}_2$  requires N =  $11.11$  per cent.)

Resolution of dl-Diphenyl- $\beta$ - $\gamma$ -diamino-n-butane.—The dl-diamine formed uncrystallisable salts with d- $\alpha$ -bromocamphor- $\pi$ -sulphonic acid, and although its d-camphor- $\beta$ -sulphonate was crystalline and separated from aqueous alcohol in needles, m.p.  $135$ – $140^\circ$ , yet the amount of resolution effected by repeated fractional crystallisation was small. It has, however, been proved that this diamine is an externally compensated base by resolving its sulpho-

nated azo-derivatives (Morgan and Skinner, 'Chem. Soc. Trans.,' 1925, vol. 127, p. 1731), and by the following resolution of its piperazine derivative.

*Meso-Diphenyl-β-γ-diamino-n-butane*.—The more soluble nitrate from the aniline and β-γ-dibromobutane condensation was converted into sulphate, the latter salt recrystallised from alcohol, and the fractions tested by benzoylation (p. 518). The fractions richest in *meso*-diamine were converted into dinitrosoamine, and this derivative was crystallised repeatedly from ether, alcohol and light petroleum.

*Meso-n-Butylene-β-γ-diphenyldinitrosoamine*, colourless crystals, m.p. 125°, was more sparingly soluble than its *dl*-isomeride in organic solvents. (Found N = 18.59.  $C_{16}H_{18}O_2N_4$  requires N = 18.79 per cent.)

Reduction of the foregoing dinitrosoamine with tin and hydrochloric acid yielded pure *meso-diphenyl-β-γ-diaminobutane*, an oily base furnishing a *dibenzoyl* derivative, m.p. 250–251°, sparingly soluble in alcohol or ether, and readily so in chloroform.

The *dihydrochloride* of the *meso*-diamine separated from alcoholic hydrochloric acid in colourless crystals. (Found Cl = 22.3.  $C_{16}H_{20}N_2 \cdot 2HCl$  requires Cl = 22.6 per cent.)

*r-1 : 4-Diphenyl-2 : 3-dimethylpiperazine*.—Ethylene dibromide and *dl*-diphenyl-β-γ-diamino-*n*-butane in molecular proportions reacted in presence of anhydrous sodium carbonate to yield *racemic* 1 : 4-diphenyl-2 : 3-dimethylpiperazine. A small amount of 1 : 4-diphenylpiperazine was also formed under special conditions. The condensation was best effected at a temperature of 115–120° for 18 to 20 hours.

The product was isolated by adding water, removing the mixture of amines by solution in benzene and precipitating the required piperazine as picrate by adding an acetone solution of picric acid. The crude picrate, after crystallisation from acetone, yielded crude *r-1 : 4-diphenyl-2 : 3-dimethylpiperazine* when decomposed by aqueous ammonia.

The externally compensated amine was obtained pure by repeated crystallisation from light petroleum or through its *d*-camphorsulphonate. It separated from petroleum (b.p. 40–60°) in groups of six-sided plates, m.p. 89–90°. (Found N = 10.92.  $C_{18}H_{22}N_2$  requires N = 10.52 per cent.)

The *picrate*, from acetone in small yellow crystals, melted and decomposed at 202–205°. (Found N = 15.63.  $C_{18}H_{22}N_2 \cdot C_6H_3O_7N_3$  requires N = 15.47 per cent.)

1 : 4-Diphenylpiperazine, a by-product in the condensation between ethylene

*dibromide and diphenyl- $\beta$ - $\gamma$ -diamino-n-butane.*—The mother liquors from the purification of crude 1 : 4-diphenyl-2 : 3-dimethylpiperazine were concentrated and mixed with ether. The precipitated picrate on decomposition with ammonia furnished a mixture of amines, which was extracted successively with small quantities of petroleum (b.p. 40-60°) and ether. The residue after crystallisation from alcohol and several times from benzene yielded a solid, m.p. 163°. Admixture with an authentic specimen of 1 : 4 diphenylpiperazine did not depress the melting point.

*Resolution of 1 : 4-Diphenyl-2 : 3-dimethylpiperazine into optically active components.*—The salt of 1 : 4-diphenyl-2 : 3-dimethylpiperazine with Reychler's *d*-camphorsulphonic acid separated from acetone in tufts of needles, m.p. 160-163° after softening from 155°. After several crystallisations from this solvent or from ethyl acetate, practically no resolution was obtained. Indeed, the impure  $\gamma$ -piperazine is conveniently purified by crystallisation of this salt from acetone.

The resolution was eventually accomplished by crystallising the salt from boiling benzene. To a solution of the amine in benzene, finely powdered *d*-camphor- $\beta$ -sulphonic acid (two mol. proportions) was added and the mixture heated till all the material had dissolved. The solution, which was evaporated till pasty owing to the separation of the salt, was filtered while still hot and the solid recrystallised several times in a similar manner.

On treatment with dilute ammonia solution the most insoluble fraction, which melted at 202-204°, yielded almost pure *dextrorotatory* 1 : 4-diphenyl-2 : 3-dimethylpiperazine. After several crystallisations from petroleum (b.p. 80-100°) the pure optically active amine was obtained in lustrous tablets, m.p. 87°;  $[\alpha]_D + 44.8^\circ$  in alcohol ( $c = 1.05$ ). (Found N = 10.93.  $C_{18}H_{22}N_2$  requires N = 10.52 per cent.)

The most soluble fractions from the systematic crystallisation of the *d*-camphorsulphonate were decomposed by aqueous ammonia and the liberated amine converted into *l*-camphorsulphonate. Crystallisation of this salt from boiling benzene in a manner described previously furnished the pure *l*-camphorsulphonate. The *levo*-rotatory amine derived from it melted at 87° and had  $[\alpha]_D - 36.8^\circ$  in alcohol ( $c = 1.10$ ). (Found N = 10.95.  $C_{18}H_{22}N_2$  requires N = 10.52 per cent.)

*The Nature of Externally Compensated 1 : 4-Diphenyl-2 : 3-dimethylpiperazine.*—Qualitative determinations of the form of the melting-point curve of mixtures of active and inactive 1 : 4-diphenyl-2 : 3-dimethylpiperazines indicated that the externally compensated amine was a true racemoid substance, the melting-



point of the active form ( $87-88^\circ$ ) being depressed to  $75-80^\circ$  by admixture with the inactive base (m.p.  $89-90^\circ$ ).\*

This conclusion was confirmed by examining artificial mixtures which had separated from suitable solvents. Approximately equal weights of *dextro*-rotatory amine and the optically inactive substance when crystallised together from light petroleum (b.p.  $80-100^\circ$ ) yielded at first fan-shaped clusters which were found on examination to be pure externally compensated 1 : 4-diphenyl-2 : 3-dimethylpiperazine (m.p.  $88-90^\circ$ ).

Spontaneous evaporation of the residual solution left an ill-defined cake of crystals, which by crystallisation from ether was resolved into a confused mass of thin transparent plates and white aggregates of needles. The plates were separated as completely as possible and recrystallised from light petroleum, when individual crystals were obtained having the characteristics of the pure active amine. When the crystals (m.p.  $86-87^\circ$ ) thus separated were mixed with those of the inactive form (m.p.  $88-90^\circ$ ) the mixture melted completely at  $81^\circ$ .

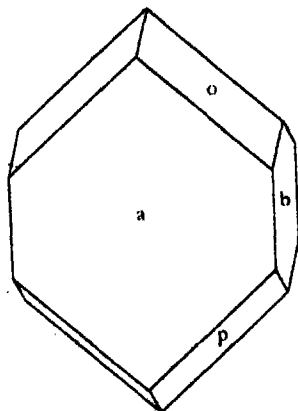


Fig. 10.

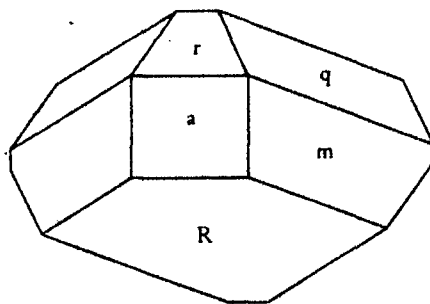


Fig. 11.

The conclusion is therefore drawn that externally compensated 1 : 4-diphenyl-2 : 3-dimethylpiperazine is a true racemoid, and this view is supported by the crystallographic evidence. The system is monoclinic with  $a : b : c = 1.750 : 1 : 0.8939$ ,  $\beta = 95^\circ 49'$ . The habit is shown in fig. 10, the forms being  $a$  (100),  $b$  (010),  $o$  (111) and  $p$  ( $\bar{1}11$ ). Following are the results of measurement of two crystals :—

\* It should perhaps be added that no significance is to be attached to this coincidence in the melting points of the active and *dl*-forms. A previous example, that of benzoyl tetrahydroquinidine, is already on record (Adriani, 'Zeit. physikal. Chem.', 1900, vol. 33, p. 469).

	<i>a</i>	<i>b</i>	<i>c</i>	<i>p</i>
$\phi$ ..	0° 0'	0° 0'	*58° 24'	*112° 22'
$\rho$ ..	90 0	0 0	*52 43	50 22 (3)

The *d*-rotatory component of the foregoing also crystallises in the monoclinic system, but the forms are more numerous and the angular values so remote that the structures are scarcely similar (a comparative X-ray examination might lead to interesting results). The habit is shown in fig. 11, the list of forms being *m* (110), *a* (100), *r* (101), *q* (011) and *R* ( $\bar{1}01$ ). The elements,  $a : b : c = 2.401 : 1 : 1.076$ ,  $\beta = 104^\circ 47'$ , were computed from the following results of measurement of two crystals:—

	<i>m</i>	<i>a</i>	<i>r</i>	<i>q</i>	<i>R</i>
$\phi$ ..	0° 0'	0° 0'	*53° 58'	75° 21' (—8)	*101° 17'
$\rho$ ..	*23 18	90 0	90 0	43 49 (3)	90 0

The authors desire to express their thanks to the Government Grant Committee of the Royal Society and to the Research Committee of the University of Birmingham for grants which have helped to defray the expense of this investigation.

### *Antimonial Analogues of the Cacodyl Series.*

By GILBERT T. MORGAN, F.R.S. and GLYN REES DAVIES.

(Received December 24, 1925.)

The fuming arsenical liquid discovered by L. C. Cadet de Gassicourt in 1760 was subsequently shown by Bunsen, Baeyer and others\* to contain cacodyl oxide  $\{(\text{CH}_3)_2\text{As}\}_2\text{O}$  and cacodyl  $\{(\text{CH}_3)_2\text{As}\}_2$ , but antimonial analogues containing the group,  $(\text{CH}_3)_2\text{Sb}$ , have not hitherto been isolated.

Of the earliest attempts to prepare organoantimonial derivatives, the most noteworthy are those of Löwig† and of Landolt,‡ who obtained respectively triethylstibine and trimethylstibine. These researches demonstrated a characteristic difference between arsenic and antimony in regard to the formation of their organic derivatives; the former element gave rise to secondary and tertiary alkyl compounds, whereas the latter furnished exclusively trialkylated products.

\* 'Liebig's Annalen,' vol. 37, p. 1 (1841); vol. 42, p. 14 (1842); vol. 46, p. 1 (1843); vol. 107, p. 257 (1858).

† *Ibid.*, vol. 75, pp. 315, 327 (1850).

‡ *Ibid.*, vol. 78, p. 91 (1851).

Berlé\* claimed to have isolated diamylstibine,  $\{(C_5H_{11})_2Sb\}_2$ , and Buckton† indicated the existence of organoantimonials containing four and five aliphatic radicals combined with an atomic proportion of antimony, but a critical examination of the records of their researches reveals an insufficiency of experimental evidence in support of the conclusions reached by these two investigators. Their products were not completely analysed—in no case were there determinations of antimony—and the chemical reactions of these dubious substances were only superficially examined.‡ So far, the only well-authenticated aliphatic alkyl antimonials belong exclusively to the tertiary stibine series.

Although overshadowed by the more outstanding characteristics of cacodyl the properties of which aroused the chemical enthusiasm of Berzelius,§ the trialkylstibines of Löwig and Landolt are also of interest in connection with the chemistry of compound radicals. Cacodyl is a unique example of an organo-metalloidal radical of uneven valency, existing in the free state only as a bimolecular complex,  $(CH_3)_2As.As(CH_3)_2$ , exhibiting univalency in its hydride  $(CH_3)_2As.H$ , chloride  $(CH_3)_2As.Cl$  and oxide  $\{(CH_3)_2As\}_2O$ , and manifesting trivalency in its trichloride  $(CH_3)_2AsCl_3$  and oxyacid  $(CH_3)_2AsO.OH$ . Trimethylstibine is an organo-metalloidal radical of even valency, existing in the free state as a monomeric substance,  $(CH_3)_3Sb$ , and displaying bivalency in its dichloride  $(CH_3)_3SbCl_2$  and oxide  $(CH_3)_3SbO$ . In a comparative study of compound and elementary radicals, cacodyl may be compared with thallium, whereas trimethylstibine may be likened to the bivalent metals of the zinc group.

Although earlier researches indicated clearly the difficulty of producing monoalkylated and dialkylated stibine derivatives, later investigations have shown that aromatic compounds of antimony are realisable containing only one or two aryl groups in association with antimony. The mono-, di- and tri-phenylstibinic acids have been studied in detail||; stibinobenzene,  $C_6H_5.Sb : Sb.C_6H_5$ , has been prepared (Fabr. Heyden, D.R.-P. 268451) and the antimonial analogue of salvarsan has been indicated (Fabr. Heyden, D.R.-P. 268451). By the experiments described below the elusive mono- and di-methylstibine derivatives have now been isolated.

\* 'Liebig's Annalen,' vol. 97, p. 316 (1856); 'J. pr. Chem.,' vol. 65, p. 385 (1855).

† 'Quart. J. Chem. Soc.,' vol. 13, p. 115 (1861).

‡ Berlé's experimental results for the supposed diamylstibine are given as follows:— $C = 45.13, 43.30, 44.83$ ;  $H = 8.88, 9.01, 8.60$ , but on recalculating these percentages the numbers for his third carbon and hydrogen estimations were found to be  $C = 47.73, H = 8.91$ , whereas the theoretical values are  $C = 45.48, H = 8.34$  per cent.

§ 'Jahresber.,' vol. 21, p. 503 (1842).

|| Michaelis and Günther, 'Ber. deutsch. chem. Ges.,' vol. 44, p. 2316 (1911); Morgan and Micklethwait, 'Chem. Soc. Trans.,' vol. 99, p. 2288 (1911).

## I. The Antimony Cacodyl Series.

The starting point in the following researches is trimethylstibine, now readily prepared by Hibbert's application of the Grignard reaction. This volatile and spontaneously inflammable compound\* is conveniently preserved in a stable form by combining it with chlorine, bromine or iodine to form the corresponding trimethylstibine dihalide.

Trimethylstibine dibromide was first applied successfully in the preparation of a dimethylantimonial, and subsequently the dichloride and di-iodide were similarly utilised.

When the dibromide is distilled under reduced pressure (90 mm.) in a current of carbon dioxide, this additive compound undergoes the following decomposition :—



The more volatile methyl bromide passes off in the carbon dioxide and *dimethylstibine bromide* is obtained as a light yellow oil which solidifies slowly to a mass of almost colourless crystals melting at 89°. This product, the antimonial analogue of cacodyl bromide, is extremely oxidisable in air and spontaneously inflammable at 50°; it removes oxygen quantitatively from a confined volume of air.

When trimethylstibine dichloride is heated in carbon dioxide under a pressure of 60 mm. it sublimes without decomposition, but on raising the pressure to 600 mm. decomposition occurs and *dimethylstibine chloride*, the analogue of cacodyl chloride, is collected as a colourless oil. This product resembles the bromide in its extreme oxidisability, being spontaneously inflammable even at 40°. The thermal decomposition of the trimethylstibine dihalides,



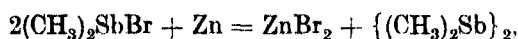
has been shown to be general for the three halogens by distilling trimethylstibine di-iodide under reduced pressure (60–80 mm.), when methyl iodide is eliminated and dimethylstibine iodide is obtained as a dark yellow oil which solidifies to a mass of bright yellow leaflets. The three trimethylstibine dihalides show a definite gradation when heated under the same pressure, namely, 80 mm.: the dichloride sublimes without decomposition, the dibromide sublimes in part but also undergoes decomposition, whereas the di-iodide is completely decomposed.

*Dimethylstibine Oxyhalides*,  $(\text{CH}_3)_2\text{SbOX}$ .—By the regulated oxidation of the

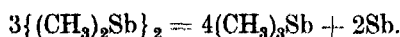
\* The trimethylstibine prepared for these experiments was also employed by Aston in demonstrating the isotopes of antimony ('Nature,' vol. 110, p. 732 (1922)).

dimethylstibine halides these substances take up an atomic proportion of oxygen forming the corresponding oxyhalides; the oxychloride and bromide are white amorphous substances, the oxyiodide is amorphous and yellow.

*Attempt to prepare Tetramethyldistibine (Antimony Cacodyl).—*Many attempts were made to remove the halogen from dimethylstibine chloride and bromide by the action of zinc, as in Bunsen's preparation of cacodyl from cacodyl chloride. The reaction which was carried out in sealed tubes in an atmosphere of carbon dioxide, proceeded far less smoothly and simply than in the arsenical series. In addition to the desired reaction,



a reversion to trimethylstibine also occurred—

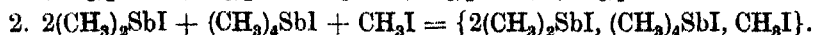


When magnesium was employed an appreciable amount of gas was generated, the increased pressure being sufficient to burst the reaction tubes.

Iron filings and copper powder were also tried, but with the same result as in the case of zinc.

The three dimethylstibine halides were tried in turn, but in no case could tetramethyldistibine be isolated in a state of purity. The di-iodide behaved similarly to the bromide, but the dichloride on reduction reverted rapidly to trimethylstibine even at the ordinary temperature.

A certain amount of the antimony cacodyl formed from the bromide was identified in the reduction product by adding methyl iodide at the ordinary temperature.\* The trimethylstibine present yielded colourless tetramethylstibonium iodide, whereas antimony cacodyl furnished a yellow molecular compound arising from the combination of dimethylstibine iodide, tetramethylstibonium iodide and methyl iodide.



This yellow complex compound has also been synthesised from its generators.

## II. Monomethylated Antimonials.

The transition from dimethylated to monomethylated derivatives of antimony is effected most readily through dimethylstibine iodide, for when this compound is treated in carbon bisulphide with sufficient iodine to produce dimethylstibine tri-iodide, absorption of the halogen occurs, but the resulting tri-iodide is unstable even at  $-15^\circ$ , so that methyl iodide is eliminated with the production of yellow crystalline *methylstibine di-iodide*  $(\text{CH}_3)_2\text{SbI}_2 = \text{CH}_3.\text{SbI}_2 + \text{CH}_3\text{I}.$

\* Compare Cahours and Riche, 'Compt. Rend.', vol. 39, p. 541 (1854).

The monomethyl series is also reached through dimethylstibine bromide which combines additively with bromine, yielding *dimethylstibine tribromide*. This product loses methyl bromide to furnish *methylstibine dibromide*.

Similarly dimethylstibine chloride combines directly with chlorine in carbon bisulphide to form dimethylstibine trichloride, which was more stable than its bromo- and iodo-analogues, but nevertheless on warming it lost methyl chloride, yielding *methylstibine dichloride*.

These monomethylated antimonials, which are not spontaneously inflammable in air, are far less oxidisable than the compounds of the dimethyl series.

Complete demethylation of methylstibine dibromide was effected by adding bromine to this substance in carbon bisulphide when antimony tribromide (m.p. 93°) separated. Methylstibine di-iodide does not combine with iodine in these circumstances, but methylstibine dichloride takes up chlorine additively, forming an oily methylstibine tetrachloride, which on warming yields antimony trichloride.

These progressive demethylations of tetramethylstibonium chloride and bromide down to inorganic antimony trichloride and tribromide respectively are analogous with the progressive demethylation of tetramethylarsonium chloride first effected by v. Baeyer.\*

#### EXPERIMENTAL.

##### I. Antimony Cacodyl Series.

Trimethylstibine was prepared by Hibbert's adaptation of the Grignard reaction.† Freshly distilled antimony trichloride (57·2 g.) dissolved in 150 c.c. of dry ether was added slowly to the Grignard reagent prepared from 18·5 g. of magnesium and 107 g. of methyl iodide dissolved in 600 c.c. of absolute ether, the mixture being cooled to — 10°. The addition of antimony trichloride produced a yellow compound which was decomposed by excess of magnesium methyl iodide, and when all the chloride had been added, the solution had a dark yellow colour. The contents of the flask were now heated in an oil bath and distilled in a current of carbon dioxide (temperature of bath 80° to 140°). The separation of trimethylstibine and ether was difficult by fractional distillation, but on adding an ethereal solution of chlorine, bromine or iodine to the distillate, the tertiary stibine was converted into the corresponding dihalide.

The dichloride and dibromide dissolved readily in hot water and crystallised from this medium in colourless needles. The di-iodide was obtained in light

\* 'Liebig's Annalen,' vol. 107, p. 282 (1858).

† 'Ber. deutsch. chem. Ges.,' vol. 39, p. 160 (1906).

yellow transparent acicular crystals less soluble than the other two dihalides in water or in alcohol. The average yield of trimethylstibine from many preparations was 55–60 per cent. calculated on antimony trichloride.

*Dimethylstibine Chloride*,  $(\text{CH}_3)_2\text{SbCl}$ .—Well-dried trimethylstibine dichloride was heated in a distilling flask under 600 mm. pressure in a current of carbon dioxide, when methyl chloride passed off in the gas and a brown oil was collected. The latter on distillation yielded a colourless liquid boiling at 155–160° under 750 mm.

(Found C = 12.52, H = 2.97, Cl = 18.92, Sb = 65.14.  $\text{C}_2\text{H}_6\text{ClSb}$  requires C = 12.81, H = 3.20, Cl = 18.95, Sb = 65.03 per cent.)

Dimethylstibine chloride had a pungent, very disagreeable odour; it was readily oxidised by slow absorption of dissolved oxygen even under a layer of light petroleum. At 40° the chloride became spontaneously inflammable in air. With platinichloric acid it gave an orange precipitate.\*

*Dimethylstibine Oxychloride*,  $(\text{CH}_3)_2\text{SbOCl}$ .—This compound was obtained when dimethylstibine chloride was allowed to oxidise slowly. The unoxidised product was covered with light petroleum and the mixture shaken occasionally until the oil had disappeared.

Dimethylstibine oxychloride, a white amorphous substance, was inodorous and moderately soluble in hot water, separating unchanged on cooling. With prolonged boiling, however, over eight hours, the oxychloride was hydrolysed, but the resulting dimethylstibinic acid was also amorphous.

Dimethylstibine oxychloride gave the following data. (Found C = 11.5, H = 2.3, Cl = 17.6, Sb = 59.6.  $\text{C}_2\text{H}_6\text{OClSb}$  requires C = 11.81, H = 2.95, Cl = 17.46, Sb = 59.9 per cent.)

*Dimethylstibine Trichloride*,  $(\text{CH}_3)_2\text{SbCl}_3$ .—A fairly rapid stream of chlorine was passed for about 10 minutes into 50 c.c. of dry carbon bisulphide which was cooled in a freezing mixture of ice and salt. About 10 gm. of dimethylstibine chloride were then added and chlorination continued until the solution began to develop a brown colour. A white crystalline compound was obtained which was collected, placed on a glass dish and rapidly dried in a vacuum desiccator. The compound was analysed as soon as it was free from carbon bisulphide (m.p. 105–110° with evolution of gas). (Found Cl = 40.75; Sb = 47.53.  $\text{C}_2\text{H}_6\text{Cl}_3\text{Sb}$  requires Cl = 41.23; Sb = 47.16 per cent.)

Dimethylstibine trichloride was more stable than the corresponding bromo-derivative, although it lost methyl chloride fairly easily, the product being a colourless oily liquid.

\* Bunsen, 'Berz. Jahresber.', vol. 21, p. 500 (1842).

*Dimethylstibine Bromide*,  $(\text{CH}_3)_2\text{SbBr}$ .—On heating trimethylstibine dibromide it was found that methyl bromide was readily evolved. Trimethylstibine dibromide (25 g.) was placed in a 50-c.c. distilling flask, to the side tube of which a small water condenser was sealed. The other end of the condenser led into another small distilling flask, which was also connected to the pump. Carbon dioxide was passed through the apparatus to remove the air and the pressure then reduced to about 80–100 mm. On heating the dibromide white fumes were at first evolved, and then a yellow oil was collected. On redistillation under the same conditions a clear limpid yellow liquid was obtained. This yellow oil was found to be very easily oxidised by air; in fact, it was spontaneously inflammable at  $50^\circ$ . The product of its regulated oxidation was a white amorphous compound. The affinity of dimethylstibine bromide for oxygen is so great that oxidation takes place even when it is kept under a liquid like light petroleum, in which the oil is not very soluble; it combines with oxygen quantitatively. (Found C = 10.55, H = 2.62, Br = 34.5, Sb = 51.83.  $\text{C}_2\text{H}_6\text{BrSb}$  requires C = 10.44, H = 2.61, Br = 34.78, Sb = 52.17 per cent.)

The freshly distilled liquid dimethylstibine bromide solidified slowly to a mass of almost colourless crystals, which at first melted somewhat indefinitely at  $40^\circ$ ; but on keeping the specimen in air-free vessels the melting point rose to  $89^\circ$ ; the boiling point was approximately  $175\text{--}180^\circ/750$  mm.

Owing to its extremely oxidisable character, dimethylstibine bromide offered considerable experimental difficulties in regard to manipulation and analytical examination.

*Analysis of Easily Oxidised Antimony Compounds* (fig. 1).—Owing to the difficulty of weighing out the dimethylstibine bromide for combustion without oxidation taking place, the apparatus shown in fig. 1 was designed for the combustion of easily oxidised or spontaneously inflammable liquids.

The apparatus having been filled with nitrogen, the stop-cocks A and B were opened, and C, D and E kept closed, the stop-cocks at the top of the U-tube being also open. A vacuum of about 60 mm. was used, and the dimethylstibine bromide or other antimonial distilled into the U-tube. The vacuum was then released with nitrogen, and enough of the bromide for a combustion run into T, the taps C, D and E being open. The tap D being closed, the small tube T was taken out, stoppers placed on both ends and weighed. The weight of the empty tube T had been previously ascertained. The stoppers were then quickly removed, the tap E opened, and the tube, after being wrapped in a little asbestos paper, was placed in an 18-mm. combustion tube.



Liquid antimonials have hitherto been oxidised with nitric acid and the antimony estimated as  $\text{Sb}_2\text{O}_4$ . The liquid antimonials obtained in this investigation reacted, however, too vigorously with nitric acid to permit of this method being used with success. Moreover, the process of weighing the ignited oxide requires very careful control over the temperature to which the  $\text{Sb}_2\text{O}_6$ — $\text{Sb}_2\text{O}_4$  mixture is heated in order to obtain only  $\text{Sb}_2\text{O}_4$ . Consequently, the following method was evolved and found to give very consistent results :—

The required amount of antimonial was weighed out and heated in a 250-c.c. beaker with 15–20 c.c. of concentrated sulphuric acid and 1–2 c.c. of nitric acid ( $D = 1.42$ ). The amount of nitric acid required varied with the percentage of carbon present in the compound to be analysed. The mixture was heated until about 4–5 c.c. of the sulphuric acid remained. When cool, the solution was diluted to 50 c.c. and 20 c.c. of concentrated hydrochloric acid were added, together with 50 c.c. of phosphoric acid ( $D = 1.3$ ). The solution was then treated with sulphuretted hydrogen at  $100^\circ$  until black antimony sulphide was obtained; 60–70 c.c. of water were added, and the gas passed in until the crystalline antimony sulphide was completely precipitated. The sulphide was filtered into a Gooch crucible, washed with sulphuretted hydrogen, and dried in the following manner :—The crucible was placed in the glass tube A, which fitted into a copper cylinder B of fig. 2. This cylinder is 20 cm. long, has an internal diameter of 3.7 cm. and is lined on the inside with thin asbestos paper. Carbon dioxide was passed in, and by means of the ring burner C the crucible was heated slowly to  $120^\circ$  for about half an hour, and then raised to  $280^\circ$ , being kept at this temperature for  $1\frac{1}{2}$ –2 hours.

*Dimethylstibine Oxybromide*,  $(\text{CH}_3)_2\text{SbOBr}$ , a white amorphous powder prepared exactly as in the case of dimethylstibine oxychloride, was moderately soluble in hot water, separating unchanged on cooling; it was slightly soluble in hot alcohol. (Found  $C = 9.43$ ,  $H = 2.30$ ,  $Br = 32.46$ ,  $Sb = 49.10$ .  $\text{C}_2\text{H}_5\text{OBrSb}$  requires  $C = 9.69$ ,  $H = 2.42$ ,  $Br = 32.28$ ,  $Sb = 49.15$  per cent.)

The aqueous solution of dimethylstibine oxybromide gave a precipitate of silver bromide with silver nitrate. Prolonged boiling with water yielded white amorphous *dimethylstibinic acid*, which was also obtained by dissolving a dimethylstibine oxyhalide in aqueous caustic soda, the solution being subsequently neutralised with dilute acetic acid. (Found  $Sb = 64.8$ .  $\text{C}_2\text{H}_7\text{O}_2\text{Sb}$  requires  $Sb = 65.9$  per cent.)

Other preparations of amorphous dimethylstibinic acid were produced by hydrolysis of the following tribromide.

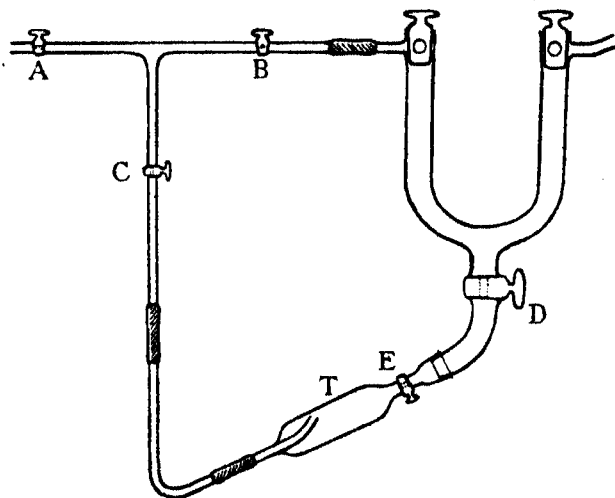


FIG. 1.

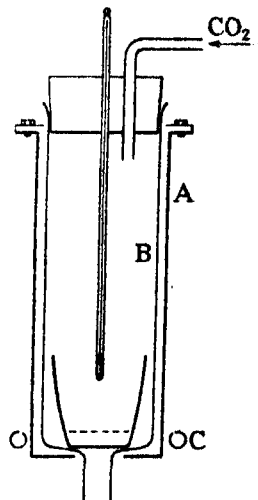


FIG. 2.

*Dimethylstibine Tribromide*,  $(\text{CH}_3)_2\text{SbBr}_3$ .—Dimethylstibine bromide was added to bromine (1 mol.) in carbon bisulphide at  $-10^\circ$  when a yellowish-white precipitate consisting of feathery needles was deposited forthwith. After quickly drying in the desiccator, it was analysed immediately. (Found Br = 60.02, Sb = 31.67.  $\text{C}_2\text{H}_6\text{Br}_3\text{Sb}$  required Br = 61.20, Sb = 31.06 per cent.)

The tribromide rapidly lost methyl bromide on keeping, becoming transformed into methylstibine dibromide.

*Bisdimethylstibine Trisulphide*,  $(\text{CH}_3)_2\text{Sb}^{\text{V}}-\text{S}-\text{Sb}^{\text{V}}(\text{CH}_3)_2$ .—A suspension



of dimethylstibine oxybromide in water was subjected to the action of a rapid stream of hydrogen sulphide. The white oxybromide was found to have changed to a light yellow precipitate with an offensive odour. The yellow product was partially soluble in carbon bisulphide. This soluble portion, which was left as a light yellow powder on evaporating the carbon bisulphide extract, was also soluble in benzene and in ammonium sulphide. It melted at  $76-78^\circ$ , and on analysis was identified as bisdimethylstibine trisulphide. (Found Sb = 60.88. Calc., 60.96 per cent.)

This compound has been previously described by Landolt,\* who obtained it indirectly by passing sulphuretted hydrogen through trimethylstibine which had been oxidised in air.

\* 'Jahresb. d. Chem. f. 1861,' p. 571 (1863).

*Dimethylstibine Iodide*,  $(\text{CH}_3)_2\text{SbI}$ .—When heated in a distilling flask under 60–80 mm. pressure, trimethylstibine di-iodide decomposed into methyl iodide and dimethylstibine iodide, the latter being collected as a dark yellow oil, which was fractionated to remove traces of methyl iodide. The redistilled dimethylstibine iodide solidified rapidly to clear yellow flaky crystals (m.p. 86). (Found C = 9.11, H = 2.24, I = 45.14, Sb = 43.78.  $\text{C}_2\text{H}_6\text{ISb}$  requires C = 8.61, H = 2.15, I = 45.55, Sb = 43.69 per cent.)

*Dimethylstibine Oxyiodide*,  $(\text{CH}_3)_2\text{SbOI}$ , a pale yellow amorphous powder produced by aerial oxidation of the foregoing iodide, was slightly soluble in hot water, and slowly hydrolysed in warm solutions. (Found C = 8.58, H = 2.25, I = 43.01, Sb = 40.93.  $\text{C}_2\text{H}_6\text{OISb}$  requires C = 8.17, H = 2.04, I = 43.04, Sb = 41.32 per cent.)

*Dimethylstibine Oxide*,  $\{(\text{CH}_3)_2\text{Sb}\}_2\text{O}$ .—When treated with aqueous caustic alkali, dimethylstibine bromide becomes converted into dimethylstibine oxide, a colourless oil which is also produced by mixing dimethylstibine bromide with a saturated aqueous solution of potassium carbonate and obtained by drying over anhydrous sodium sulphate, the colourless oil being then filtered through glass wool. (Found Sb = 76.6.  $\text{C}_4\text{H}_{12}\text{OSb}_2$  requires Sb = 76.2 per cent.) This oily oxide was spontaneously inflammable in air at the ordinary temperature.

*Attempt to prepare Tetramethylstibine (Antimony Cacodyl)*.—Dimethylstibine bromide was heated with zinc (Kahlbaum's No. 1) in sealed tubes filled with carbon dioxide. Zinc bromide was produced together with antimony, the product containing trimethylstibine and some antimony cacodyl. On distilling this liquid product in carbon dioxide, trimethylstibine was identified in the more volatile fraction by its boiling point and the following analyses. (Found C = 20.8, H = 5.2, Sb = 73.5.  $\text{C}_3\text{H}_9\text{Sb}$  requires C = 21.6, H = 5.3, Sb = 73.0 per cent.)

The antimony cacodyl could not be separated from the less volatile fractions because of its decomposition into trimethylstibine and antimony, but it was identified by adding methyl iodide to the oily mixture. A light yellow crystalline product separated, which was re-crystallised from alcohol when the first crops consisted of a yellow substance A, and the final mother liquors yielded colourless needles of tetramethylstibonium iodide. (Found I = 41.30.  $\text{C}_4\text{H}_{12}\text{ISb}$  requires I = 41.1 per cent.) Substance A, was crystallised repeatedly from alcohol and obtained finally in bright yellow needles or leaflets. (Found C = 10.93, H = 2.89, I = 50.54, 50.3, 51.0, Sb = 36.1, 36.3, 35.9.  $\text{C}_9\text{H}_{27}\text{I}_4\text{Sb}_3$  requires C = 10.71, H = 2.68, I = 50.5, Sb = 36.2 per cent.) The composition of the foregoing molecular compound as  $\{2(\text{CH}_3)_2\text{SbI}, (\text{CH}_3)_4\text{SbI}, \text{CH}_3\text{I}\}$  was con-

firmed by adding to excess of methyl iodide one molecular proportion of tetramethylstibonium iodide and two molecular proportions of dimethylstibine iodide. After repeated crystallisation the synthetic product separated in yellow needles and leaflets and gave  $C = 10.3$ ,  $H = 2.7$ ,  $I = 50.63$ ,  $Sb = 35.4$ . An ebullioscopic determination of molecular weight in glacial acetic acid ( $c = 1.04$ ) gave  $M = 970$ , whereas  $C_6H_{27}I_4Sb_3$  requires  $M = 1003$ .

## II. Monomethylated Stibine Derivatives.

*Methylstibine Dichloride*,  $CH_3SbCl_2$ .—This compound was obtained when dimethylstibine trichloride was heated in a vacuum of about 600 mm. until all the methyl chloride had been evolved. The resulting oil was then distilled under a pressure of 60 mm., the boiling point of the oil being between 115 and 120° at this pressure. The oil did not solidify even after keeping for some days in an ice chest. It was easily decomposed by water, yielding methylstibine oxide. (Found  $C = 6.21$ ;  $H = 1.74$ ,  $Sb = 58.16$ ,  $Cl = 34.51$ .  $CH_3Cl_2Sb$  requires  $C = 5.77$ ,  $H = 1.44$ ,  $Sb = 58.60$ ,  $Cl = 34.17$  per cent.)

*Methylstibine Dibromide*,  $CH_3SbBr_2$ .—On leaving dimethylstibine tribromide in the desiccator this crystalline substance became viscid with loss of methyl bromide, and the residue finally resolidified to greyish-white feathery needles. This product when recrystallised from carbon bisulphide and ether yielded greyish-white needles melting at 42°. (Found  $C = 3.7$ ,  $H = 0.92$ ,  $Br = 54.7$ ,  $53.73$ ,  $Sb = 40.53$ .  $CH_3Br_2Sb$  requires  $C = 4.04$ ,  $H = 1.01$ ,  $Br = 53.91$ ,  $Sb = 41.04$  per cent.)

Methylstibine dibromide is non-inflammable and non-oxidisable in air, but is hydrolysed in water or alkaline solutions.

*Methylstibine Di-iodide*,  $CH_3SbI_2$ , which arises from the spontaneous decomposition of dimethylstibine tri-iodide crystallised from carbon bisulphide in rosettes of bright yellow needles melting at 110°. (Found  $C = 3.18$ ,  $H = 0.78$ ,  $I = 65.2$ ,  $Sb = 31.7$ .  $CH_3I_2Sb$  requires  $C = 3.07$ ,  $H = 0.77$ ,  $I = 65.0$ ,  $Sb = 31.20$  per cent.)

The di-iodide was very soluble in hot carbon bisulphide, ether or benzene, dissolving more sparingly in light petroleum; stable in air, it was hydrolysed very slowly with hot water.

*Methylstibine Sulphide*,  $CH_3SbS$ .—The action of sulphuretted hydrogen on any of the monomethyl antimonials resulted in the formation of a lemon yellow precipitate. This substance, when dried, was found to be slightly soluble in carbon bisulphide and benzene. The product obtained from either of these solvents was an amorphous yellow powder which fused at about 70° to a resinous mass. (Found  $Sb = 71.4$ .  $CH_3SSb$  requires  $Sb = 72.16$ .)

*Methylstibine Oxide*,  $\text{CH}_3\text{SbO}$ .—This substance was best prepared by agitating methylstibine dichloride with water, the solution being kept neutral by the occasional addition of dilute alkali. A white amorphous product was obtained, but the analytical results were not good. It was proved to be methylstibine oxide by acting on it with hydriodic acid, when methylstibine di-iodide was produced.

### *Dimethylstibine Cyanide, an Analogue of Cacodyl Cyanide.*

By GILBERT T. MORGAN, F.R.S., and VICTOR E. YARSLEY.

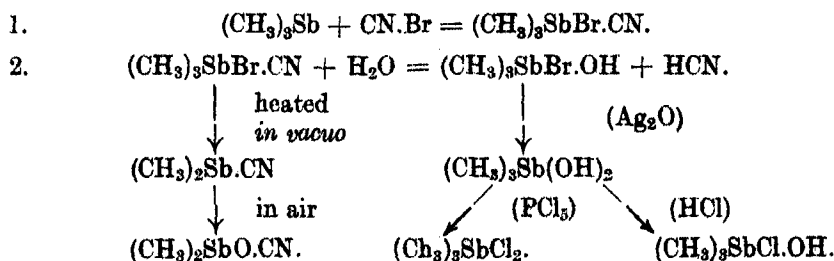
(Received December 24, 1925.)

The combination of cyanogen bromide and organic arsines has been studied by Steinkopf and collaborators,\* who found that triethylarsine furnished an unstable cyanobromide hydrolysed by air to triethylarsine hydroxybromide, although the unhydrolysed product, triethylarsine cyanobromide, was eventually isolated in a special apparatus.†

Aliphatic and aliphatic-aromatic arsines combine similarly with cyanogen bromide to form arsine cyanobromides, and these additive products when heated lose alkyl bromide with the formation of the corresponding cacodyl cyanides.

Experiments on trimethylstibine described below have led to the isolation of *dimethylstibine cyanide*, the antimonial analogue of the cacodyl cyanide first described by Bunsen.‡ Trimethylstibine forms a characteristic cyanobromide by combination with cyanogen bromide in ethereal solution. Exposed to moist air this trimethylstibine cyanobromide is readily hydrolysed to *trimethylstibine hydroxybromide*, but when heated under reduced pressure at  $160\text{--}180^\circ$ , the cyanobromide undergoes thermal decomposition, losing methyl bromide and yielding dimethylstibine cyanide as a colourless crystalline solid.

The following scheme summarises the reactions subsequently described:—



\* 'Ber. deutsch. chem. Ges.,' vol. 54, pp. 841, 2791 (1921); vol. 55, p. 2597 (1922).

† Wolfram, 'Ber. deutsch. chem. Ges.,' vol. 54, p. 857 (1921).

‡ 'Liebig's Analen,' vol. 37, p. 23 (1841).

*Experimental.*

Owing to the spontaneously inflammable nature of trimethylstibine and to the instability of its derivatives in moist air, the experiments were carried out in the closed apparatus shown in the figure described below.

Trimethylstibine was prepared in this apparatus by distilling trimethylstibine dibromide\* with Kahlbaum's pure zinc (No. 1).

Cyanogen bromide, obtained by the interaction of bromine and potassium cyanide in aqueous solution at 60–70°, was dried by distillation over calcium chloride and phosphoric oxide.

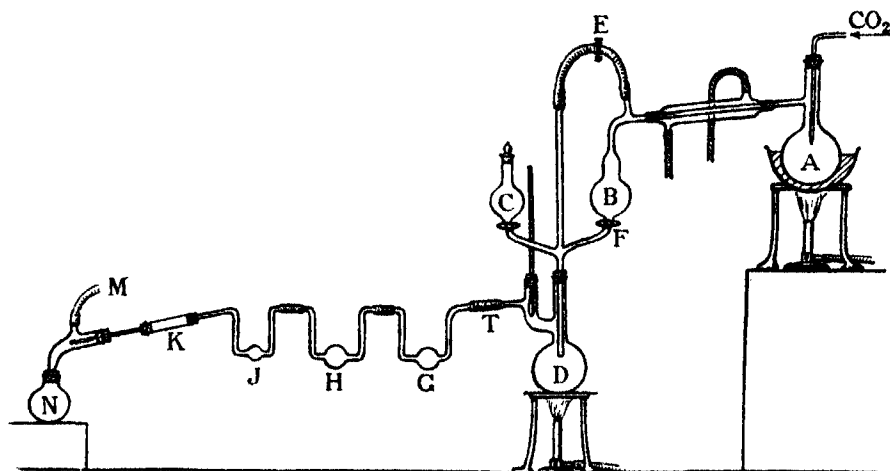


FIG. 1.

*Trimethylstibine cyanobromide*,  $(\text{CH}_3)_3\text{SbBr.CN}$ .—Calculated amounts of cyanogen bromide dissolved in petroleum (b.p. 40–60°) were introduced through the tap funnel C into distillation flask D, this vessel being cooled to  $-5^\circ$ . Nitrogen or carbon dioxide was passed through the apparatus to displace air; trimethylstibine was then distilled gradually from the flask A into receiver B, and thence it was added in appropriate quantity and with constant shaking to the cyanogen bromide in flask D. The solid product was then collected and analysed immediately. (Found: Sb, 44.7; N (Kjeldahl), 4.9.  $\text{C}_4\text{H}_9\text{NBrSb}$  requires Sb, 44.7; N, 5.1 per cent.)

*Trimethylstibine cyanobromide* was a colourless crystalline solid, insoluble in cold anhydrous organic media but hydrolysed very rapidly by moisture to yield the hydroxybromide.

\* Hibbert, 'Ber. deutsch. chem. Ges.', vol. 39, p. 160 (1906).

### 536 *Dimethylstibine Cyanide, an Analogue of Cacodyl Cyanide.*

*Dimethylstibine cyanide*,  $(\text{CH}_3)_2\text{Sb.CN}$ .—The foregoing cyanobromide being prepared as before in the air-free apparatus, the taps E and F were closed and the light petroleum removed from flask D by distillation. The distillate was either collected in N or removed from the apparatus by gentle aspiration at tap M. During this operation care was taken to keep the condensing bulbs G, H, J and K free from deposited oxide. The apparatus was then exhausted to about 10 mm. pressure, and the flask D containing trimethylstibine cyanobromide was gradually heated to about  $160^\circ$ , when decomposition of the cyanobromide set in and a colourless deposit separated in the first bulb G, the intervening tube T, which was packed with glass-wool, being warmed by several coils of resistance wire. The bulk of the product which had collected in the first bulb G was then re-sublimed into the second bulb H, and this operation repeated so that the solid product of the thermal decomposition was finally collected in a pure condition in the weighed glass cylinder K. By opening the screw clip E nitrogen or carbon dioxide was admitted, the cylinder K was removed, fitted with rubber stoppers and weighed, air being excluded during this operation. In this way a weighed quantity of the product was isolated in a container readily adaptable to analytical requirements. (Found: C, 20.4; H, 3.38; N, 7.7; Sb, 67.8.  $\text{C}_3\text{H}_6\text{NSb}$  requires C, 20.2; H, 3.38; N, 7.9; Sb, 68.5 per cent.)

*Dimethylstibine cyanide*, m.p.  $113\text{--}114^\circ$ , a colourless crystalline compound, had the nauseating odour of volatile aliphatic antimonials, but beyond a slight irritant action on the eyes and respiratory passages its effects were not appreciably toxic. Insoluble in water, it readily dissolved in ether or alcohol.

*Dimethylstibine oxycyanide*,  $(\text{CH}_3)_2\text{SbO.CN}$ .—Dimethylstibine cyanide readily underwent oxidation in the air, yielding the oxycyanide as a white crystalline compound sintering slightly at  $120^\circ$  and decomposing completely at higher temperatures. (Found: Sb, 62.1.  $\text{C}_3\text{H}_6\text{ONSb}$  requires Sb, 62.6 per cent.)

*Trimethylstibine hydroxybromide*,  $(\text{CH}_3)_3\text{Sb(OH).Br}$ , a white crystalline compound, was formed with great rapidity by the hydrolysis of trimethylstibine cyanobromide; it was readily soluble in cold water and separated from alcoholic solution in lustrous white needles decomposing without melting. (Found: C, 14.1; H, 4.1; Br, 30.7; Sb, 45.9.  $\text{C}_3\text{H}_{10}\text{OBrSb}$  requires C, 13.8; H, 3.8; Br, 30.7; Sb, 45.8 per cent.)

*Trimethylstibine dihydroxide*,  $(\text{CH}_3)_3\text{Sb(OH)}_2$ , prepared by warming 2 g. of the hydroxybromide with 1 g. of silver oxide in 10 c.c. of water on the water bath for one hour, separated from the filtrate in colourless microscopic crystals slightly hygroscopic but otherwise stable. (Found: Sb, 58.5.  $\text{C}_3\text{H}_{11}\text{O}_2\text{Sb}$  requires Sb, 58.6 per cent.)

With an aqueous solution of picric acid this dihydroxide gave a well-defined pale yellow hydroxypicrate. When gently warmed with phosphorous pentachloride in slight excess, trimethylstibine dichloride was obtained in well-defined colourless needles. (Found Sb, 50.7. Calculated Sb, 51.2 per cent.)

*Trimethylstibine hydroxychloride*,  $(\text{CH}_3)_3\text{SbCl.OH}$ , was precipitated as a white flocculent mass on adding concentrated hydrochloric acid to an aqueous solution of the foregoing dihydroxide. (Found: Cl, 16.7; Sb, 55.3. Calculated Cl, 16.4; Sb, 55.5 per cent.)

The hydroxychloride was soluble in water; it crystallised from ether in minute colourless plates and from alcohol in silky needles.

One of us (V.E.Y.) desires to express his thanks to the Salters' Institute of Industrial Chemistry for a Fellowship which has helped to defray the expense of this investigation.

*Researches on the Chemistry of Coal—Part IV. The Oxidation of the Residue from the Benzene-Pressure-Extraction Process.*

By WILLIAM A. BONE, D.Sc., F.R.S., and R. QUARENDON, B.Sc., D.I.C., Beit Research Fellow.

(Received December 19, 1925.)

Since publishing the last paper of this series,\* in which was described our process of extracting coals with benzene under pressure up to 700 lb. per square inch, and of fractionating the crude extracts thereby obtained, we have turned our attention to the "residues" resulting from it, which in the case of most bituminous coals usually form about 90 per cent. of the actual coal substance. And in this paper the results of our experiments during the past eighteen months upon their oxidation by means of an alkaline solution of potassium permanganate are briefly described.

It was decided to publish these results at this stage of the investigation because of the recent publication by Mr. W. Francis and Prof. R. V. Wheeler of an account of their work upon "The Properties and Constitution of Coal Ulmins,"† in the course of which they oxidised, with either hydrogen peroxide or 30 per cent. nitric acid, what they termed the "regenerated ulmins from coals,"

\* 'Proc. Roy. Soc.,' A, vol. 105, pp. 608-625 (1924).

† 'Trans. Chem. Soc.,' vol. 127, pp. 2237-2245 (1925).



obtaining good yields of oxalic and succinic acids together with small quantities of other acids, among which picric acid, and certain benzene polycarboxylic acids were mentioned. They state (*loc. cit.*, p. 2245) "symmetrical benzene tetracarboxylic acid (m.p.  $264^{\circ}$  with decomposition) has been isolated in a pure form by slow crystallisation from acetic acid, and its methyl ester (m.p.  $138^{\circ}$ ) formed. The tricarboxylic acid appears to be trimellitic acid, but it has not yet been obtained in a sufficiently pure crystalline form to identify." No ultimate analyses of these acids were, however, published.

In the course of our work we have found it possible, by means of alkaline permanganate, to oxidise and effect the complete solution of the "residue" from the benzene-pressure-extract of a bituminous coal so as finally to produce therefrom a yellow crystalline mass of acidic oxidation products amounting to between 25 and 40 per cent. of the weight of the coal-residue taken.

The task of isolating and purifying the numerous acid constituents of such a complex oxidation product is not an easy one, and considerable losses of material have necessarily been entailed in our explorative procedure; these will, no doubt, be largely avoided in repetition work, after we have gained a fuller knowledge of the principal types of acids present. Nevertheless, we have already obtained from 260 grams of the crude oxidation product about 10 grams of purified mellitic acid, and there is evidence of at least 20 more grams of this substance yet to come. Also 1.2.3.4 benzene tetracarboxylic acid has been isolated. Besides these, we have already obtained (but not identified) about 25 grams of other acids, and there are still larger quantities in sight.

In this connection it should be mentioned that in recent years F. Fischer and his collaborators have made experiments upon the oxidation of coal, either by means of ozone when passed through liquids in which the coal was suspended, or by means of air at  $250^{\circ}$  C. at 50 atmospheres pressure. In the last-named case, the bituminous coal yielded small percentages of various aromatic acids, among which benzoic (0.4 per cent.), phthalic and trimesic (0.9 per cent.), isophthalic (0.3 per cent.), mellitic and benzene pentacarboxylic (0.6 per cent.) acids were identified.

The larger yields of such acids as we have obtained, under the conditions referred to, obviously have an important bearing upon the chemical structure of the coal substance; in particular, the considerable yield of mellitic acid in our experiments shows it to contain rings of 6 carbon atoms, to each of which other carbon atoms are connected.

## EXPERIMENTAL.

*A. Oxidation of the Benzene-Pressure-Extracted Coal Residue.*

1,140 grams of the dried benzene-pressure-extracted residue from the Durham Coking Coal A used in this investigation (*vide* Part III, Table I, *loc. cit.*, p. 614), in a finely ground condition, were mixed in an autoclave with 13,680 grams of pure potassium permanganate, 800 grams of potassium hydroxide and 17.5 litres of water. The autoclave was then closed up, and its temperature slowly raised to 70° C., its contents being stirred all the time. On attaining this temperature the source of heat (an external gas flame) was cut off, because the heat of the resulting oxidation became more than sufficient to complete it. Thus in the first of two experiments, in which separate batches of the materials were handled, the temperature of the liquid rose to about 140° C., whilst in the second it rose to 175° C., the final gauge pressure attained in the latter case being as much as 140 lb. per square inch. On opening the autoclave at the end of the operation, no gas-pressure was discernible, such CO<sub>2</sub> as had been formed during the oxidation having been absorbed by the potassium hydroxide present.

The resulting cold liquor from the oxidation, containing much hydrated oxides of manganese in suspension, was next centrifuged, and the clear liquor so obtained was thereupon acidified with hydrochloric acid, and as a preliminary examination had shown the absence of volatile acids, the liquor was next evaporated nearly to dryness in a steam pan, with frequent additions of concentrated hydrochloric acid, and removals of the potassium chloride as it crystallised out. The drying was completed *in vacuo* over solid potassium hydroxide.

The organic acids present in the dried residue were subsequently extracted by means of (1) ether, and (2) acetone, in the order named. The two (ether and acetone) solutions were next separately dried over anhydrous sodium sulphate, and the solvents evaporated. The resulting mixtures of acids on being united for further treatment were found to amount to 260 grams, or about 25 per cent. of the weight of the original coal-residue taken.\*

The mixed acids resulting from the oxidation process, after being dried *in vacuo*, were left behind as a light yellow flaky hygroscopic solid, which could be easily powdered; it was all soluble in water, and for the most part in alcohol also.

\* In a preliminary experiment, however, in which about 80 grams of the "coal-residue" were used, the yield of mixed acids was 32 grams (*i.e.* 40 per cent.).

An attempt was made to estimate the average molecular weight by the ebullioscopic method, using acetone as solvent; it appeared to be as high as 400, but the figure must be regarded as subject to unknown error on account of uncertain behaviour of the acids in such solution. Nevertheless, it indicates the presence in the mixture of acids of high molecular aggregation, the isolation and identification of which will throw further light upon the constitution of the coal substance.

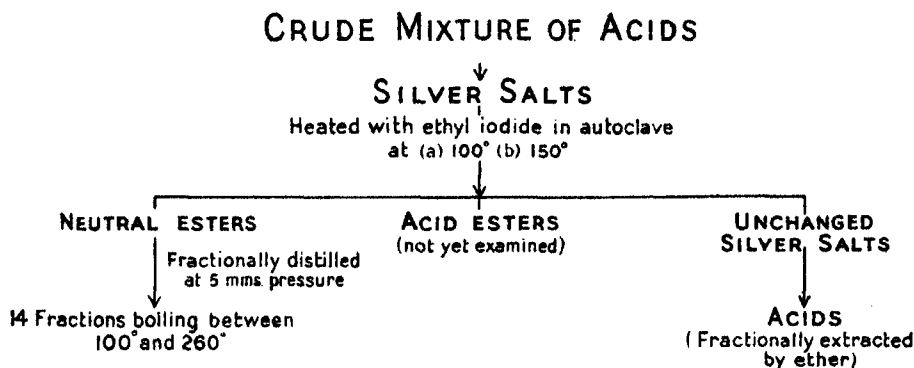
*B. Fractionation of the Resulting Acids.*

A fractionation of the mixed acids has been carried out, up to a certain point, in accordance with the following plan:—The mixture was first of all dissolved in water and the solution neutralised with ammonia; sufficient of silver nitrate was then added to produce the silver salts of the acids present. Most of these were at once thrown down as a light brownish precipitate, but a small part remained in solution. The whole was evaporated to dryness, and the residue subsequently reduced to powder by grinding it in a mortar. The finely pulverised silver salts were next esterified by heating them in suspension in ether with three times the theoretical quantity of ethyl iodide, the operation being conducted in a sealed autoclave in two stages, namely, first of all at 100° (twice), and finally at 150° C. (twice). As the result of this treatment, approximately two-fifths of the mixed acids were esterified, for the most part being converted into neutral esters, although some acid esters were also produced. The ethereal solution containing these esters was thereupon filtered off from the unchanged silver salts, which, after being further washed with ether, were reserved for further investigation.

On recovering the mixed esters from the ethereal solution in the usual manner, they were washed with sodium carbonate solution for the extraction of any acid esters which they might contain. The neutral esters remaining were subsequently fractionally distilled under a pressure of about 5 mm.; altogether 11 different fractions were obtained, at various temperature ranges between about 100° and 260°, together with a considerable residue boiling above the last-named point.

These various neutral ester-fractions were next separately hydrolysed by means of a 25 per cent. hydrochloric acid. The acid-esters, which are nearly solid, have not as yet been examined in detail. The unesterified silver salts have been reconverted into the corresponding acids, which, after a fractional extraction of their aqueous solution by ether, are now being investigated. The

general scheme of fractionation of the acids resulting from the oxidation of the coal-residue is shown in the accompanying diagram.



From the neutral ester fractions, five different acids have already been isolated. The chief of these is 1.2.3.4. *benzene tetracarboxylic acid*, melting with decomposition between 235 and 237° C. Its composition has been established by analysis as follows :—

	Found.	Calculated.
C .. .. .	46·8	47·1
H .. .. .	2·4	2·4
Equivalent .. .. .	63·4	63·5

A second acid, which melts in the first instance with decomposition at 144° C., is probably *propane α β tricarboxylic acid*, which has similar properties ; but the quantity so far obtained has been too small to permit of its complete identification.

The three other acids so far obtained from the neutral esters melt respectively (a) at 199–200°, (b) at 236°, and (c) at 195·5 to 197·5° C., but they have not yet been identified. The acid-esters, which are of small amount, have yet to be examined.

From the unchanged silver salts, considerable quantities of mellitic acid (*benzene hexacarboxylic acid*) have already been isolated. The acid thus obtained melts at the same temperature (279° C.) as a specimen of the synthetic acid kindly given us by Dr. M. A. Whiteley ; and a mixture of the two melted at exactly the same temperature. Its “equivalent” has been found to be 57·7 as compared with the theoretical value of 57·0.

Two other acids, one melting between 190 and 195° C., and the other

between 202 and 208° C., have also been isolated, but they have yet to be purified before their identities can be established.

*Concluding Remarks.*

(1) It is, of course, well known that mellitic acid is produced by oxidising charcoal with fuming nitric acid, or by electrolysing alkaline solutions using graphite electrodes; but this is (we believe) the first time that it has been produced in quantity by the oxidation of coal in circumstances which preclude the formation of a 6-carbon ring structure. Hence it may be concluded that coal actually contains such 6-ring structure.

(2) The complete investigation of the complex mixture of acids resulting from such oxidation experiments as have been described herein, and the working out of the many other possibilities which are thereby opened up, will necessarily occupy us for a considerable time.

(3) In a recent paper by one of us (W. A. B.) on the "Constitution of Coal,"\* it was urged that "*inasmuch as coal is a complex colloidal organic substance, of high molecular aggregation, the task of elucidating its chemical constitution should be entrusted to the organic chemist,*" and that "*we would do well to import more organic chemists into our fuel laboratories, and to rely more and more upon the systematic methods of organic chemical research.*" And it is hoped that the line of attack upon the "coal constitution," by the methods similar to those indicated herein, may interest organic chemists.

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\* 'Journ. Soc. Chem. Industry,' vol. 44, pp. 291T-299T (1925).

*On the Law and Mechanism of Monomolecular Reaction.*

By S. C. ROY, M.Sc., King's College, Physical Research Laboratory, London.

(Communicated by Professor O. W. Richardson, F.R.S.—Received  
September 19, 1925.)

1. The object of the present paper is to work out an expression for the rate of monomolecular reaction on the basis of the idea that radiation is the cause of such reactions. The whole position of the radiation hypothesis of chemical reactivity up till now has been fully discussed by Harned.\* I only wish to draw attention to the fact, as pointed out by Langmuir,† and Lewis and McKeown,‡ that a great similarity exists between photo-electric emission of electrons and photo-chemical reaction. The true analogue of the thermo-chemical reaction should be sought, however, in the phenomenon of thermionic emission of electrons. It has long been shown experimentally by Richardson and others that the thermionic emission of electrons is vastly in excess of the total photo-electric emission at any temperature  $T$ . In the same way we should expect that the amount of thermo-chemical reaction in a system at a given temperature should be greater than the total photo-chemical reaction by black body radiation at the same temperature. Becker§ has shown that the distribution of velocities among the photo-electrons emitted from a metal by the action of black body radiation at a temperature  $T$  is similar to that found amongst the electrons emitted thermally from the hot metal at the same temperature  $T$ . It is thus natural to assume that the thermionic emission of electrons from a hot body is really due to the radiation in equilibrium with it. Richardson|| has recently given a very interesting discussion on the photo-electric theory of thermionic emission of electrons. Owing to the well-known difficulties the old view of the freely-moving electrons in a metal has, in recent years, been replaced by that of a lattice structure—a metal being considered to be constituted of interlaced lattices of ions and electrons. Such a view of metallic electrons precludes them from sharing in kinetic energy according to the equipartition law. It is rather more rational to imagine that the metallic electrons do exist in some modified quantum

\* 'J. Franklin Institute,' vol. 196, p. 181 (1923).

† 'J. Am. Chem. Soc.,' vol. 42, p. 2506 (1920).

‡ This 'Journal,' vol. 43, p. 1288 (1921).

§ 'Ann. Physik,' vol. 60, p. 30 (1919).

|| 'Proc. Phys. Soc.,' London, vol. 36, p. 383 (1924).

orbits, and are bound to the ions by a certain potential energy. If this view of the electronic structure in metals be accepted, then we have to look to radiation as the only controlling factor in the emission of electrons from hot bodies. The writer\* has tried to show that the law of thermionic emission derived on the basis of radiative mechanism is in good agreement with experiment. Lewis and McKeown† have pointed out that "the concept of matter and radiation being at one and the same temperature means that as a result of absorption and emission, the system as a whole maintains a certain distribution of energy among all frequencies." If by some process a set of frequencies are removed the system tends to make good the loss by a corresponding reverse process, provided the velocity of the process be not too large to make it physically impossible to keep the system at a fixed temperature by means of a thermostat. In my view the resemblance of photo-electric emission and photo-chemical reaction with thermionic emission and thermo-chemical reaction respectively arises from both kinds of processes being due to radiation. But the distinction‡ lies in the fact that one is due to the action of *high* temperature radiation on a *cold* system, while the other is brought about by the action of radiation in temperature *equilibrium* with the system itself.

## 2. *The Range of Frequencies of Radiation capable of bringing about a Chemical Reaction.*

Up till now it has been usually assumed that a single frequency, or rather a narrow range of frequencies, is capable of bringing about a chemical change. But experiments have shown that photo-chemical reactions are produced by the action of light of a wide range of frequencies. The simplest of all chemical reactions is the breaking up of atoms into ions and electrons, and it is widely known that the photo-electric action in various elements, both in solid and vapour phase, are brought about by all frequencies of radiation above a certain limiting frequency. The familiar reaction of practical photography is also known to be produced by light of a great variety of wave-lengths. It is, therefore, evident that a more complete theory of chemical reactivity should involve a summation of a number of frequencies, or, what is more plausible, an integration over a whole range of frequencies above a certain limiting value.

\* 'Phil. Mag.,' vol. 50, p. 250 (July, 1925), and 'Proc. Ind. Ass. Cult. Sc.,' vol. 9, part 1, p. 61 (1924).

† *Loc. cit.*

‡ The writer hopes to discuss this point more fully in another paper.

Tolman\* realised the importance of this phase of the problem in his application of statistical mechanics to chemical reactivity, but failed to get a definite expression for the specific thermal rate of monomolecular reaction owing to some difficulties inherent in his method of treatment.

### 3. *The Present View-Point of Chemical Reactivity.*

From what has been discussed in the foregoing pages it is clear that the problems of chemical reactivity and radiation are very closely linked together. It is, therefore, necessary in a study of the kinetics of chemical reaction in a system of molecules to adopt some hypothesis as to the mechanism of energy-exchange between the system and the bath of radiation in which it is placed. We shall appeal to Einstein's concept of emission and absorption of radiation by matter for a working basis of the present problem.

Let us consider a molecule AB constituted of two parts A and B, which are held together probably by a link between the valence-electrons. The dissociation of the molecule involves a tearing apart of the bonds between these electrons. Let  $\phi$  be the work necessary to shatter the molecule into its parts. We shall suppose that the absorption of a quantum of radiation  $h\nu$  (sufficiently large to provide for energy  $\phi$ ) by a molecule AB, results in its explosion, and its components A and B shoot out in opposite directions along the line of their centres. If the velocities shared by the masses  $m_A$  and  $m_B$  be adjusted by the law of conservation of momentum, then the relative velocity  $v$  of separation of the particles is given by

$$\frac{1}{2} \cdot \left( \frac{m_A \cdot m_B}{m_A + m_B} \right) \cdot v^2 = h\nu - \phi. \quad (1)$$

The extension of Einstein's law of photo-electric effect to the disruption of molecules may be questioned. But the writer finds no *a priori* reason why it should not apply to the case† of uncharged particles.

Next we suppose that the reverse process of formation of a molecule AB results from a "head-on" collision between A and B approaching each other with a relative velocity  $v$ , and is attended by the consequent emission of the "light-quant,"

$$h\nu = \phi + \frac{1}{2} \left( \frac{m_A \cdot m_B}{m_A + m_B} \right) \cdot v^2. \quad (2)$$

\* 'J. Am. Chem. Soc.,' vol. 42 (1920).

† Cf. O. W. Richardson's discussion on a similar point given in his book, 'Electron Theory of Matter,' 2nd ed., p. 473 (1916).



In the stationary state of temperature radiation, the two reverse processes ( $AB \rightleftharpoons A + B$ ) are controlled by the unit-mechanism

$$h\nu \rightleftharpoons \frac{1}{2}\mu v^2 + \phi, \quad (3)$$

where  $\mu$  is the "reduced mass" equal to  $\left(\frac{m_A \cdot m_B}{m_A + m_B}\right)$ .

The principle that every isolatable process is exactly compensated in a state of thermal equilibrium by precisely the same process working backwards, is believed to be a general principle which governs various physical and chemical changes. The concept of unit-mechanism has, lately, been applied in various ways by Klein and Rosseland,\* Kramers,† Milne,‡ Fowler,§ Richardson|| and the present writer¶ to different problems with success.

Owing to our ignorance of the exact mechanism by which a molecule takes up a radiation-quantum and gives it out, we cannot directly calculate the probabilities of the two reverse processes. We can, however, find out a relation between the two probabilities by making use of Einstein's idea of emission and absorption of radiation by atoms.

#### 4. Deduction of the Law of Monomolecular Reaction.

In this chapter the molecules are considered normally to be in a "reactive state." The more general type of chemical dissociation involving an initial "loosening of the chemical bonds" in the molecules to make them ready for reaction will be discussed in the next chapter.

For simplicity let us confine our attention to a single molecule AB contained in a "Hohlraum" of volume  $V$  and temperature  $T^\circ A$ . We can apply Boltzmann's principle,\*\* and obtain a relation between the probability  $P_.$

\* Klein and Rosseland, 'Z. für Phys.,' vol. iv, p. 46 (1921).

† 'Phil. Mag.,' vol. 46, p. 836 (1923).

‡ 'Phil. Mag.,' vol. 47, p. 209 (1924).

§ 'Phil. Mag.,' vol. 47, p. 257 (1924).

|| *Loc. cit.*

¶ *Loc. cit.*

\*\* (Cf. Jeans, 'Dynamical Theory of Gases,' 2nd ed., 1916, p. 210, chapter on the "Degree of Aggregation.") Let us take  $(x, y, z)$  to represent positional co-ordinates and  $(\alpha, \beta, \gamma)$  to represent velocity co-ordinates. According to Boltzmann's generalisation of Maxwell's distribution law, the probability that a particle with energy  $\epsilon$  has its representative-point in the phase-space  $d\tau \cdot dO$  is given by the expression,

$$\left(\frac{m}{2\pi kT}\right)^{3/2} \cdot e^{-\epsilon/kT} d\tau \cdot dO \quad (1)$$

where

$$\left. \begin{aligned} d\tau &= dx \cdot dy \cdot dz \\ dO &= d\alpha \cdot d\beta \cdot d\gamma \end{aligned} \right\}.$$

The simultaneous probability that the particle A with energy  $\epsilon_A$  shall find its representative-

point in the phase-space  $d\tau_A \cdot dO_A$ , while the particle B with energy  $\epsilon_B$  has its representative-point in the phase-space  $d\tau_B \cdot dO_B$  is,

$$\omega_{AB} = \frac{(m_A \cdot m_B)^{3/2}}{(2\pi kT)^3} \cdot e^{-(\epsilon_A + \epsilon_B)/kT} \cdot d\tau_A \cdot d\tau_B \cdot dO_A \cdot dO_B. \quad (II)$$

Let  $(l_1, l_2, l_3)$  be the velocity-components of the centre of gravity of the pair of particles A and B, and  $(v_1, v_2, v_3)$  be the components of their relative velocity, so that,

$$\left. \begin{aligned} l_1 &= \frac{m_A \cdot \alpha_A + m_B \alpha_B}{m_A + m_B}, \text{ \&c.} \\ v_1 &= (\alpha_A - \alpha_B), \text{ \&c.} \end{aligned} \right\} \quad (III)$$

And it can also be easily verified that,

$$\frac{\partial (l_1, v_1)}{\partial (\alpha_A, \alpha_B)} = 1, \text{ \&c.} \quad (IV)$$

Hence, (V)  
 $dO_A \cdot dO_B = dl_1 \cdot dl_2 \cdot dl_3 \cdot dv_1 \cdot dv_2 \cdot dv_3.$

Similarly, if  $(s_1, s_2, s_3)$  be the positional co-ordinates of the centre of gravity of the pair and  $(q_1, q_2, q_3)$  their relative co-ordinates of position, then

$$d\tau_A \cdot d\tau_B = dq_1 \cdot dq_2 \cdot dq_3 \cdot ds_1 \cdot ds_2 \cdot ds_3. \quad (VI)$$

The total energy of the pair is,

$$\begin{aligned} (\epsilon_A + \epsilon_B) &= \frac{1}{2} (m_A + m_B) (l_1^2 + l_2^2 + l_3^2) + \frac{1}{2} \left( \frac{m_A \cdot m_B}{m_A + m_B} \right) (v_1^2 + v_2^2 + v_3^2) + W_{AB} \\ &= \frac{1}{2} (m_A + m_B) (l_1^2 + l_2^2 + l_3^2) + \left( \frac{1}{2} \mu v^2 + W_{AB} \right). \end{aligned} \quad (VII)$$

Where  $W_{AB}$  stands for the potential energy of the pair. Further, since no external force is supposed to act on the pair of particles, their energy with respect to the co-ordinates of the centre of gravity is invariable.

Also (VIII)  

$$\left. \begin{aligned} \int_{-\infty}^{+\infty} e^{-\frac{1}{2}(m_A + m_B)(l_1^2 + l_2^2 + l_3^2)} dl_1 \cdot dl_2 \cdot dl_3 &= \left( \frac{2\pi kT}{m_A + m_B} \right)^{3/2} \\ \text{and} \int ds_1 \cdot ds_2 \cdot ds_3 &= V \end{aligned} \right\}$$

Hence, we have, finally, the probability,

$$\omega_{AB} = C \cdot e^{-(\frac{1}{2}\mu v^2 + W_{AB})/kT} dq_1 \cdot dq_2 \cdot dq_3 \cdot dv_1 \cdot dv_2 \cdot dv_3 \quad (IX)$$

where

$$C = V \cdot \frac{(m_A \cdot m_B)^{3/2}}{(2\pi kT)^3} \cdot \left( \frac{2\pi kT}{m_A + m_B} \right)^{3/2} \quad (X)$$

$$= V \cdot \left( \frac{\mu}{2\pi kT} \right)^{3/2}. \quad (XI)$$

(1) When the molecule AB is dissociated, the potential energy,  $W_{AB} = 0$ , and also since

$$\int dq_1 \cdot dq_2 \cdot dq_3 = V$$

and

$$dv_1 \cdot dv_2 \cdot dv_3 = v^2 dv \cdot \sin \theta \cdot d\theta \cdot d\psi,$$

the probability that the molecule AB is dissociated into its components A and B which

such that the molecule is in its normal undissociated state, and the probability  $P_n$ , such that it is dissociated into its components which move with a relative velocity between  $v$  and  $v + dv$ .

These probabilities are related to each other as follows :—

$$\begin{aligned} P_n : P_v &= C \cdot e^{\phi/kT} \cdot \frac{ah^3}{\mu^3} : 4\pi C \cdot V \cdot e^{-\frac{1}{2}\mu v^2/kT} \cdot v^2 \cdot dv \\ &= ah^3 \cdot e^{(\phi + \frac{1}{2}\mu v^2)/kT} : 4\pi V \mu^3 v^2 \cdot dv, \end{aligned} \quad (4)$$

where  $a$  is the statistical weight of the undissociated state of the molecule.

Next we define a probability-coefficient  $\alpha_v$  such that the chance that in a given interval of time the molecule under the action of radiation of frequency between  $\nu$  and  $\nu + d\nu$  undergoes decomposition in such a way that its constituents are expelled with a relative velocity lying between  $v$  and  $v + dv$  is\*

$$Q_{n \rightarrow v} \cdot dt = \frac{4\pi\alpha_v \cdot K_\nu \cdot d\nu \cdot dt}{h\nu} \quad (5)$$

where  $K_\nu$  is the specific intensity of radiation of frequency  $\nu$ .  $\alpha_v$  has the dimension of an area and may be interpreted as the cross-section of the effective "sphere of action" between a molecule and a light quant  $h\nu$  for a kind of inelastic collision which brings about an explosion of the molecule freely with a relative velocity between  $v$  and  $v + dv$  in a volume  $V$  quite independent of the directions of motion, is

$$Pv = 4\pi C \cdot e^{-\frac{1}{2}\mu v^2/kT} \cdot v^2 \cdot dv. \quad (XII)$$

(2) In the undissociated state of the molecule AB the two components are relatively at rest and are bound together with a potential energy  $W_{AB} = -\phi$ .

Also writing  $(p_1, p_2, p_3)$  for the relative momenta co-ordinates of the pair, we have

$$p_1 = \left( \frac{m_A \cdot m_B}{m_A + m_B} \right) v_1 = \mu v_1,$$

and so on. Hence,

$$dq_1 \cdot dq_2 \cdot dq_3 \cdot dv_1 \cdot dv_2 \cdot dv_3 = \frac{dq_1 \cdot dq_2 \cdot dq_3 \cdot dp_1 \cdot dp_2 \cdot dp_3}{\mu^3}.$$

We then suppose with Planck that the elementary phase-space

$$dq_1 \cdot dp_1 \cdot dq_2 \cdot dp_2 \cdot dq_3 \cdot dp_3 = ah^3,$$

where  $a$  is the statistical weight of the undissociated state of the molecule AB. Thus, we obtain the probability

$$P_n = C \cdot e^{\phi/kT} \cdot \frac{ah^3}{\mu^3} \quad (XIII)$$

\* The chance of decomposition is taken proportional to half the density of unpolarised radiation, since at any instant only those "light-quanta" which are going to be absorbed are effective in bringing about decomposition.

cule, and its components shoot out with a relative velocity  $v$  given by equation (1).

We shall next suppose that the reverse process of formation of a molecule by collision between its component parts with emission of radiation, is controlled by the sum of two distinct probabilities: (1) one is independent of the radiation, and (2) the other is proportional to the intensity of radiation  $K_\nu$ . Let  $\beta_\nu$  denote the effective "collision area" for unstimulated recombination of the constituents and  $\beta'_\nu K_\nu$  denote the effective "collision area" for stimulated recombination; so that  $(\beta_\nu + \beta'_\nu K_\nu)$  represents the total effective "collision area" for recombination of the components with emission of radiation. Thus the probability that in a given time interval  $dt$ , the two components colliding with each other with a relative velocity  $v$  shall result in the formation of the normal molecule with emission of radiation is equal to

$$Q_{v \rightarrow n} \cdot dt = \frac{(\beta_\nu + \beta'_\nu K_\nu) \cdot v \cdot dt}{V} \quad (6)$$

In the steady state of equilibrium we have

$$P_n \cdot Q_{n \rightarrow v} = P_v \cdot Q_{v \rightarrow n} \quad (7)$$

or, making use of the relations (4), (5) and (6) in (7), and putting

$$\phi + \frac{1}{2}\mu v^2 = h\nu \quad \text{and} \quad \frac{dv}{dv} = \frac{\mu v}{h},$$

we have,

$$\frac{ahx_\nu \cdot K_\nu}{v} \cdot e^{h\nu/kT} = \mu^2 v^2 (\beta_\nu + \beta'_\nu K_\nu), \quad (8)$$

i.e.,

$$K_\nu = \frac{\frac{\beta_\nu}{\beta'_\nu}}{\frac{ah}{\mu^2 v^2} \cdot \frac{\alpha_\nu}{\beta'_\nu} \cdot e^{h\nu/kT} - 1} \quad (9)$$

Comparing the expression (9) with Planck's expression

$$K_\nu = \frac{h\nu^3}{c^2} \cdot \frac{1}{e^{h\nu/kT} - 1} \quad (10)$$

we obtain,

$$\left. \begin{aligned} \frac{\alpha_\nu}{\beta'_\nu} \frac{ah}{\mu^2 v^2} &= 1 \\ \frac{\beta_\nu}{\beta'_\nu} &= \frac{h\nu^3}{c^2} \end{aligned} \right\} \quad (11)$$

From (11)

$$\frac{\alpha_\nu}{\beta_\nu} = \frac{c^2 \mu^2 v^2}{ah^2 \nu^2} \quad (12)$$

Also the ratio of the number of stimulated recombinations to the number of unstimulated recombinations is given by

$$\frac{\beta'_\nu K_\nu}{\beta_\nu} = \frac{1}{e^{h\nu/kT} - 1}. \quad (13)$$

Within the range of frequencies capable of bringing about chemical changes, the number of stimulated recombinations is vanishingly small. Hence we can take  $\beta_\nu$  as representing the "total effective area" for a recombination-encounter between A and B. The relation (12) can be given a physical meaning by writing

$$\left. \begin{aligned} \beta_\nu &\propto \frac{1}{(\mu v)^2} \\ \alpha_\nu &\propto \frac{1}{\left(\frac{h\nu}{c}\right)^2} \end{aligned} \right\} \quad (14)$$

i.e., the "effective area"  $\beta_\nu$  of recombination encounter between the two chemical constituents of a molecule is inversely proportional to the square of the relative momentum of impact, while the "cross section"  $\alpha_\nu$  of the effective "sphere of action" between a molecule and a "light-quant" during an inelastic collision varies inversely as the square of the momentum of the light-quant. The second conclusion is equivalent to the supposition\* that the radius of the "sphere of action" of a light quant is proportional to the wave-length.

According to the present view of the rupture of a molecule, the reaction  $AB \rightleftharpoons A + B$  runs independent of the concentration of the molecules. Hence for N molecules the number of decompositions in time  $dt$  by radiation of frequencies between  $\nu$  and  $\nu + d\nu$  is obtained simply by multiplying expression (5) by N.

We shall now suppose that instead of a single frequency, or rather a small range of frequencies, the whole spectrum of radiation of frequencies higher than a certain critical value  $\nu_0 = \phi/h$ , is effective in producing a chemical reaction. On this supposition we obtain for the total rate of dissociation of the molecules,

$$-\frac{d}{dt} N_{AB} = N_{AB} \cdot \frac{4\pi}{h} \int_0^\infty \frac{K_\nu \cdot \alpha_\nu \cdot d\nu}{\nu}. \quad (15)$$

\* Lewis ('Phil. Mag.,' vol. 39, p. 26 (1920)) has made a tentative attempt to explain chemical reactivity on the basis of the idea that a quantum has a radius equal to that of an electron. But Rideal ('Phil. Mag.,' vol. 40, pp. 461-465, (1920)) has concluded that the size of a quantum is equal to its wave-length.

Introducing the values of  $\alpha_v$  and  $K_v$  in (15), we obtain the following expression for the velocity constant of a monomolecular reaction :

$$\begin{aligned} K_1 &= - \frac{1}{N_{AB}} \cdot \frac{d}{dt} N_{AB} \\ &= \frac{4\pi\mu^2}{ah^2} \int_0^\infty \beta_v \cdot v^2 \cdot \frac{dv}{e^{h\nu/kT} - 1}. \end{aligned} \quad (16)$$

No progress can, however, be made with the relation (16) unless some assumption is adopted about the "collision area"  $\beta_v$ , which is clearly a function of  $v$ . In the absence of any knowledge about the functional relation between  $\beta_v$  and  $v$  we shall suppose that the interpretation of  $\beta_v$  given in (14) is real, and that the product  $\beta_v \cdot v^2$  is a constant equal to  $q$ . Also, if the frequencies of radiation capable of producing chemical changes be so high as to make  $e^{h\nu/kT}$  large compared to unity, then from (16)

$$\begin{aligned} K_1 &= \frac{4\pi\mu^2 q}{ah^2} \int_0^\infty e^{-h\nu/kT} dv \\ &= \frac{4\pi \cdot \mu^2 \cdot q}{ah^3} \cdot k \cdot T e^{-h\nu_0/kT} \end{aligned} \quad (17)$$

We shall now try to estimate the constant  $q$  by considering the velocity of the reverse process of formation of molecules AB by collision between A and B. The reverse reaction is a bi-molecular process and its velocity is determined by the frequency of collisions between A and B. The rate of formation of AB by collision between A and B with relative velocities lying between the range  $v$  and  $v + dv$  is given by the expression\*

$$\begin{aligned} \frac{d}{dt} \cdot N_{AB} &= N_A \cdot N_B \cdot \beta v \left( \frac{2\mu^3}{\pi k^3 T^3} \right)^{\frac{1}{2}} \cdot e^{-\frac{1}{2}\mu v^2/kT} v^3 \cdot dv \\ &= N_A \cdot N_B \cdot \left( \frac{2\mu^3}{\pi k^3 T^3} \right)^{\frac{1}{2}} \cdot q \cdot e^{-\frac{1}{2}\mu v^2/kT} v \cdot dv, \end{aligned} \quad (18)$$

where  $N_A$  and  $N_B$  are the number of A and B per unit volume.

Let us now suppose that the constant  $q$  is equal to the product of the average values of  $v^2$  and  $\beta_v$  during collisions between A and B, i.e.,

$$q = v^2 \cdot \beta_v = \bar{v}^2 \cdot \bar{\beta}_v = \text{constant}. \quad (19)$$

Now the average value of  $v^2$  during collisions between A and B is given by

$$\bar{v}^2 = \frac{q \int_0^\infty v^2 \cdot e^{-\frac{1}{2}\mu v^2/kT} v \cdot dv}{q \int_0^\infty e^{-\frac{1}{2}\mu v^2/kT} v \cdot dv} = \frac{2kT}{\mu}. \quad (20)$$

\* Jeans, 'Dynamical Theory of Gases,' 2nd ed., p. 267 (1916), equation (737).

Since  $v^2$  varies directly as  $T$ , and  $\bar{\beta}_v \cdot \bar{v}^2$  is supposed to be a constant independent of  $T$ ,  $\bar{\beta}_v$  must vary inversely as  $T$ , that is

$$\bar{\beta}_v = \frac{\bar{\beta}_0}{T}. \quad (21)$$

Hence

$$q = \bar{\beta}_v \cdot \bar{v}^2 = \frac{2k}{\mu} \cdot \bar{\beta}_0. \quad (22)$$

Introducing this value of  $q$  in (17) we obtain finally for the velocity constant of a mono-molecular reaction

$$K_1 = -\frac{1}{N_{AB}} \frac{d}{dt} \cdot N_{AB} = \frac{8\pi\mu k^2}{h^3} \cdot \frac{\bar{\beta}_0}{a} \cdot T \cdot e^{-h\nu_0/RT}. \quad (23)$$

It is easily verified that this relationship is dimensionally correct.

Writing,

$$\left. \begin{aligned} Q_0 &= Nh\nu_0 \\ R &= Nk \end{aligned} \right\} \quad (24)$$

and

$$K_1 = \frac{8\pi\mu k^2}{h^3} \cdot \frac{\bar{\beta}_0}{a} \cdot T \cdot e^{-Q_0/RT}. \quad (25)$$

Where  $N$  is the Avogadro-number, and  $Q_0$  is the "molecular heat of dissociation."

### 5. Reaction Involving "Activation."

In the foregoing pages it is, tacitly, assumed that the dissociating molecules are normally in a state to react. But one can easily extend the above calculations to include the more general type of reactions involving a preliminary "activation" before decomposition by a radiation quantum  $h\nu > h\nu_0$ .

The expressions "activation" and "heat of activation" are often used in a very wide sense. An "activated" molecule is said to be identical with its decomposition products. The so-called "heat of activation" signifies, usually, the "total heat of decomposition" of a normal molecule into its components.

The present writer has thought it fit to use these words in a more restricted sense. The word "activation" here implies the process by which a normal molecule comes to a "reactive" state, such that the absorption of a radiation-quantum  $h\nu > h\nu_0$  by the molecule in this state results in its disruption. To avoid confusion, the following notations are used in this chapter:—

$$\text{Molecular "heat of dissociation" } Q_0 = Nh\nu_0 \quad (1)$$

$$\text{Molecular "heat of activation" } Q_a = Nh\nu_a \quad (2)$$

$$\text{Molecular "total heat of reaction" } Q_t = (Q_a + Q_0), \quad (3)$$

where  $\nu_0$  is the "threshold frequency" for chemical dissociation, and  $\nu_a$  is the "activating" frequency.

The process involved in the more general type of chemical reactions are symbolically represented by the scheme :—



The symbols  $[ ]_n$  and  $[ ]_a$  signify the "normal" and the "active" states respectively.

The rate at which the normal molecules break up, is determined by the rate at which the "activated" molecules dissociate into active constituents. Hence by relation (23) of § 4

$$-\frac{d}{dt}[N_{AB}]_n = [N_{AB}]_a \cdot \frac{8\pi\mu k^2}{h^3} \cdot \frac{\bar{\beta}_0}{p_a^{AB}} \cdot T \cdot e^{-h\nu_a/kT}, \quad (5)$$

where  $p_a^{AB}$  is the statistical weight of the "activated" state of the molecule AB.

Now according to Boltzmann's principle,

$$\frac{[N_{AB}]_a}{[N_{AB}]_n} = \frac{p_a^{AB}}{p_n^{AB}} \cdot e^{-(\epsilon_a - \epsilon_n)/kT}, \quad (6)$$

where  $p_a^{AB}$  and  $p_n^{AB}$  are the statistical weights, and  $\epsilon_a$  and  $\epsilon_n$  are the energies of the corresponding states of the molecules. Let  $(\epsilon_a - \epsilon_n) = h\nu_a^{AB}$ , where  $\nu_a^{AB}$  is the "activating" frequency. The "activation" of a molecule to the final state in which it is ready to dissociate by absorption of a radiation-quantum  $h\nu > h\nu_0$  is, presumably, brought about through a number of stages. But the number of molecules in the final "reactive" state is independent of the number of "activating" stages passed through, and is solely determined by relation (6). It is, therefore, a matter of indifference to the derivation of a law of mono-molecular reaction whether or not the molecules pass through a series of quantised states before reaching the final "reactive" state. It is sufficient to know only the energy difference  $(\epsilon_a - \epsilon_n)$  between the "normal" and the final "reactive" state. The writer, however, points out the possibility that the "activating" frequency  $\nu_a^{AB}$  may be a sum of a number of frequencies corresponding to some absorption lines of the molecules.

From (17) and (18)

$$\begin{aligned} K_1 &= -\frac{1}{[N_{AB}]_n} \cdot \frac{d}{dt}[N_{AB}]_n \\ &= \frac{p_a^{AB}}{p_n^{AB}} \cdot \frac{8\pi\mu k^2}{h^3} \cdot \frac{\bar{\beta}_0}{p_a^{AB}} \cdot T \cdot e^{-h(\nu_a^{AB} + \nu_0)/kT} \\ &= \frac{8\pi\mu k^2}{h^3} \cdot \frac{\bar{\beta}_0}{p_n^{AB}} \cdot T \cdot e^{-(Q_a^{AB} + Q_0)/RT}. \end{aligned} \quad (7)$$



In the case of reactions involving no initial activation,  $Q_a^{AB} = 0$ ; and so the total "heat of reaction" is just equal to the "heat of dissociation."

The sum of the frequencies ( $\nu_a^{AB} + \nu_0$ ) may be treated as a single frequency in numerical calculations with this law. Let ( $\nu_a^{AB} + \nu_0$ ) be equal to  $\nu_{AB}$ . We might call  $\nu_{AB}$  the "effective frequency of reaction" of a molecule AB. We should, however, regard  $\nu_{AB}$  only as a virtual frequency, and it would be futile to look for an absorption-band in the molecule at a frequency  $\nu_{AB}$ .

#### 6. Agreement of the Law with Experimental Data.

For purposes of numerical computations the law may be put in the form,

$$K_1 = S \cdot T \cdot e^{-b/T}, \quad (1)$$

where,

$$S = \frac{8\pi k^2 \cdot m_H}{h^3} \left( \frac{A \cdot B}{A + B} \right) \cdot \frac{\bar{\beta}_0}{a}, \quad (2)$$

and

$$b = \frac{Q_a^{AB} + Q_0}{RT} = \frac{h(\nu_a^{AB} + \nu_0)}{kT} = \frac{h\nu_{AB}}{kT}. \quad (3)$$

A and B are the molecular weights of the parts of the decomposing molecule and  $m_H$  is the mass of a hydrogen atom, and  $a$  is the statistical weight of the normal state of the molecule AB.

Taking,

$$k = 1.37 \times 10^{-16} \text{ erg/degree.}$$

$$h = 6.56 \times 10^{-27} \text{ erg/sec.}$$

$$m_H = 1.66 \times 10^{-24} \text{ gram.}$$

$$S = 2.774 \times 10^{24} \cdot \left( \frac{A \cdot B}{A + B} \right) \cdot \frac{\bar{\beta}_0}{a}. \quad (4)$$

Also taking logarithm of (1), and arranging,

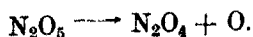
$$(\log_{10} T - \log_{10} K_1) = \frac{b}{2.303} \cdot T^{-1} - \log_{10} S. \quad (5)$$

The graph obtained by plotting values of  $(\log_{10} T - \log_{10} K_1)$  against  $T^{-1}$  should be a straight line. The intercepts of this line on the two axes determine  $b$  and  $\frac{\bar{\beta}_0}{a}$ .

#### (A) Reactions in Gases.

(1) The only clear case of a monomolecular gaseous reaction recorded is the decomposition of nitrogen-pentoxide. The measurements were first done by

Daniels and Johnston.\* The experiment has been, very lately, repeated by White and Tolman.† Their measurements bear out the conclusions of the first experimenters, namely, that the dissociation rate of  $N_2O_5$  is proportional to the first power of the pressure of the gas, and is independent of the surface of the containing vessel.



$$\frac{A \cdot B}{A + B} = \frac{92 \times 16}{108} = 13.62.$$

The values of the velocity constants given by Daniels and Johnston agree very closely with those of White and Tolman. The plots of  $(\log_{10}T - \log_{10}K_1)$  against  $T^{-1}$  obtained from Daniels and Johnston's data lie on a perfect straight line and we get

$$\left. \begin{aligned} b &= 12200 \\ \frac{\beta_0}{a} &= 1.83 \times 10^{-15} \end{aligned} \right\}$$

$$\log_{10}K_1 = 10.8389 + \log_{10}T - \frac{5298}{T}.$$

$T^{\circ}A.$	$K_1 \times 10^5 \text{ sec}^{-1}.$ (Obs. by D and J.)	$K_1 \times 10^5 \text{ sec}^{-1}.$ (Obs. by W. and T.)	$K_1 \times 10^5 \text{ sec}^{-1}.$ (Cal.)
298	3.38	3.65	3.41
308	13.5	13.9	13.4
318	49.5	—	48.0
328	150	—	160
338	487	—	487

The agreement between experiment and the present law is quite satisfactory in the case of decomposition of  $N_2O_5$ .

(2) Trautz and Bhandarkar,‡ and Krooy have reported the decomposition of phosphine to be monomolecular. But since then Hinshelwood and Topleys§ have repeated the experiment and found it to be heterogeneous. There is little doubt that the decomposition of  $PH_3$  is liable to "catalytic effect." In

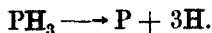
\* Daniels and Johnston, 'J. Am. Chem. Soc.,' vol. 43, p. 53 (1921).

† White and Tolman, 'J. Am. Chem. Soc.,' pp. 1240-1255 (May, 1925).

‡ 'Z. Anorg. Chem.,' vol. 106, pp. 81-127 (1919), and vol. 120, p. 81 (1918).

§ 'J. Chem. Soc.,' vol. 125, p. 393 (1924).

the absence of any other available data, the writer has also tried to test the applicability of the present law in the case of decomposition of  $\text{PH}_3$ .



$$\frac{A \cdot B}{A + B} = \frac{3 \times 31}{34} = 2.676.$$

$$\left. \begin{array}{l} b = 30740 \\ \frac{\bar{\beta}_0}{a} = 0.4 \times 10^{-15} \end{array} \right\}$$

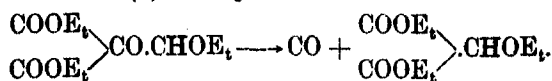
$$\log_{10} K_1 = 9.4599 + \log_{10} T - \frac{13340}{T}.$$

$T^\circ\text{A}.$	$K_1 \times 10^5 \text{ sec.}^{-1} (\text{obs.})$		$K_1 \times 10^5 \text{ sec.}^{-1} (\text{cal.})$
719	0.081	} Krooy	0.063
745	2.1		2.6
845	54		43
918	360	} Trautz and Bhandarkar	830
956	2200		4500

The writer is not acquainted with any more precise determinations of  $K_1$  for gaseous dissociation. Watson\* has, very recently, shown that the thermal decomposition of the derivatives of oxalacetic esters is mono-molecular. It is shown below that the present law agrees well with his data.

(B) *Reactions in Solutions.*

(1) *Ethoxy-Oxalacetic Ester.*



$$\frac{A \cdot B}{A + B} = \frac{28 \times 204}{232} = 24.62.$$

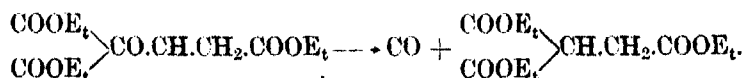
$$\left. \begin{array}{l} b = 17,340 \\ \frac{\bar{\beta}_0}{a} = 1.361 \times 10^{-14} \end{array} \right\}$$

$$\log_{10} K_1 = 11.9682 + \log_{10} T - \frac{7530}{T}.$$

$T^\circ\text{A}.$	$K_1 \times 10^4 \text{ sec.}^{-1} (\text{obs.})$	$K_1 \times 10^4 \text{ sec.}^{-1} (\text{cal.})$
446	52.4	52.4
451	85.5	84.0
456.5	138.5	128.5
461	204.0	199.0
466	266.0	306.0

\* 'Roy. Soc. Proc.,' A, vol. 108, p. 132 (1925).

(2) Oxal-Succinic Ester.



$$\frac{A.B}{A+B} = \frac{28 \times 246}{274} = 25.14.$$

$$\left. \begin{array}{l} b = 17460 \\ \frac{\bar{\beta}_0}{a} = 5.78 \times 10^{-14} \end{array} \right\}$$

$$\log_{10} K_1 = 12.6055 + \log_{10} T - \frac{7578}{T}.$$

$T^{\circ}\text{A.}$	$K_1 \times 10^4 \text{ sec}^{-1} \text{ (obs.)}$	$K_1 \times 10^4 \text{ sec}^{-1} \text{ (cal.)}$
423	20.5	21.4
433	54.7	60.7
443	138.6	138.7

7. Concluding Remarks.

It will be noticed that  $\frac{\bar{\beta}_0}{a}$  is of the order of the cross-section of a molecule, and is large for complicated organic molecules. This is what is expected. According to the assumption  $\bar{\beta}_e = \frac{\bar{\beta}_0}{T}$ ,  $\bar{\beta}_0$  may be theoretically defined as the average "effective area" for a re-combination encounter by the components at  $1^{\circ}\text{A}$  and physically interpreted as the sum of the cross-sections of the two colliding parts of the molecule, since at  $1^{\circ}\text{A}$  the molecules are closely packed together, and each part of a molecule may be looked upon as presenting its whole area to that of the other for combination.

It is unfortunate that one does not know at present what values to attach to the statistical weight factor  $a$  introduced here. The writer ventures to suggest that the weight  $a$  is determined by the number of valency-bonds between the two parts of the molecule, and that each bond has weight 2. The reason for ascribing weight 2 to each bond instead of one is that a single link between two atoms involves two valence electrons. The suggestion, however, is only a tentative one and must be regarded as such. Some figures are given in support of this contention as follows :—

Reactions.	$\frac{\bar{E}_0}{a}$	No. of bonds.	$a$	$\bar{E}_0$	Molecular radius.
1. $N_2O_4 \longrightarrow N_2O_2 + O$	$1.83 \times 10^{-13}$	$\equiv O$	4	$7.32 \times 10^{-13}$	$4.8 \times 10^{-8}$
2. $_3PH_3 \longrightarrow _3H + P$	$4.0 \times 10^{-13}$	$\equiv P$	6	$2.4 \times 10^{-13}$	$2.7 \times 10^{-8}$
*3. $COCl_2 \longrightarrow Cl_2 + CO$	$3 \times 10^{-13}$	$\equiv C=O$	4	$12 \times 10^{-13}$	$6.1 \times 10^{-8}$
4. $COOEt \begin{cases} \longrightarrow CO \cdot CHOEt \\ \longrightarrow CO + COOEt \end{cases}$ $COOEt \begin{cases} \longrightarrow CO \cdot CHOEt \\ \longrightarrow CO + COOEt \end{cases}$ $COOEt \begin{cases} \longrightarrow CO \cdot CHOEt \\ \longrightarrow CO + COOEt \end{cases}$	$1.36 \times 10^{-14}$	$\equiv C-O-$ or $\equiv C=O (?)$	8	$10.9 \times 10^{-14}$	$1.7 \times 10^{-7}$
5. $COOEt \begin{cases} \longrightarrow CO \cdot CH_2CH_2COOEt \\ \longrightarrow CO + COOEt \end{cases}$ $COOEt \begin{cases} \longrightarrow CO \cdot CH_2CH_2COOEt \\ \longrightarrow CO + COOEt \end{cases}$ $COOEt \begin{cases} \longrightarrow CO \cdot CH_2CH_2COOEt \\ \longrightarrow CO + COOEt \end{cases}$	$5.78 \times 10^{-14}$	„	8	$46.2 \times 10^{-14}$	$3.8 \times 10^{-7}$

\* Computed from the approximate data quoted by Dushman, 'Journ. Am. Chem. Soc.,' vol. 43, p. 417 (1921).

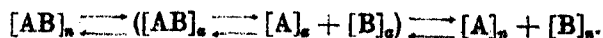
The figures in the last column lend support to the idea of associating the weight  $a$  with valence-bonds. It is hoped that the idea may be fruitful in future, when more data on the subject are available.

A discussion on the "heat of activation"  $Q_a^{AB}$  and the "heat of dissociation"  $Q_0$  is reserved for a second paper dealing with chemical equilibrium and velocity of the reverse process of re-combination.

### 7. Summary.

The introductory part of the paper contains a discussion on the rôle of radiation in photo-chemical and thermo-chemical reactions, and also in the allied phenomena of photo-electric and thermionic emission of electrons. It is emphasized that the action of *high* temperature radiation on a *cold* system cannot be *quantitatively* the same as the action of radiation on a system in temperature *equilibrium* with it.

Two types of mono-molecular reactions are considered: (1) one in which the molecules are normally "reactive," (2) the other in which the molecules require preliminary "activation." The first type of reaction is a particular case of the more general one, which is represented symbolically as follows:—



The two reverse processes of dissociation and re-combination of reactive molecules ( $[AB]_a \rightleftharpoons [A]_a + [B]_a$ ) is supposed to be governed by the unit mechanism,  $h\nu \rightleftharpoons \frac{1}{2}\mu v^2 + \phi$ , where  $\mu$  is the "reduced" mass equal to  $\frac{m_A \cdot m_B}{m_A + m_B}$ , and  $v$  is the relative velocity with which the two components of the molecule shoot out by absorption of a radiation quantum. The radiation effective in producing dissociation of the "reactive" molecules is supposed to consist of the whole range of frequencies above a certain critical value  $\nu_0 = \phi/h$ . The molecules, probably, pass through a number of stages of "activation" before reaching the final "reactive" state, but the reaction-velocity is dependent only on the energy-difference between the "normal" and the final "reactive" state. The expression obtained for the specific rate of mono-molecular reaction is

$$K_1 = -\frac{1}{[N_{AB}]_n} \cdot \frac{d}{dt} [N_{AB}]_n = \frac{8\pi k^2 m_H}{h^3} \cdot \left( \frac{A \cdot B}{A + B} \right) \cdot \frac{\bar{\beta}_0}{a} T \cdot e^{-(Q_a^{AB} + Q_0)/RT}.$$

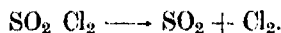
Where A and B are the molecular weights of the components.  $\bar{\beta}_0$  is identified with the cross-section of the reacting molecule.  $a$  is a statistical *weight* factor, which is determined by the number of valency-bonds between the components.  $Q_a^{AB}$  is the "molecular heat of activation" of the molecule AB, and  $Q_0$  is the "heat of dissociation" of the reacting molecule. The law is shown to agree well with existing experimental data on mono-molecular reactions of molecules in the gaseous state as well as in solution.

In conclusion, the writer records his indebtedness to Prof. O. W. Richardson for many helpful suggestions and criticism.

[*Note added on November 30, 1925.*—Since the present paper was written, Tolman ('*Jour. Am. Chem. Soc.*,' vol. 47, p. 1524 (1925) and Lewis and Smith ('*this Journal*,' vol. 47, p. 1508 (1925) have published two interesting theoretical papers on mono-molecular reactions. Space would not permit me to discuss them fully. But attention may be drawn particularly to Tolman's discussion on the relative speeds of "activation" and "reaction," and also to the conclusions of Lewis and Smith, namely, that (i) the radius of the "sphere of action" of a "light-quant" is proportional to the wave-length, and that (ii) the "single frequency" theories of chemical reactivity are in general inadequate to explain thermal reaction rates.

David Smith ('*Jour. Am. Chem. Soc.*,' vol. 47 p. 1862 (July, 1925)) has

recently shown that the thermal decomposition of gaseous sulphuryl chloride is a first order homogeneous reaction. The results of his measurements are given below and appear to be in fair agreement with the present law of monomolecular reaction.



$$\frac{A \cdot B}{A + B} = \frac{64 \times 71}{135} = 33.67.$$

$$\left. \begin{array}{l} b = 24730 \\ \frac{\beta_0}{\alpha} = 3 \times 10^{-14} \end{array} \right\}.$$

$$\log_{10} K_1 = 12.4474 + \log T - \frac{b}{2.303 T}.$$

$T^{\circ}\text{A.}$	$K_1 \times 10^5 \text{ sec}^{-1}$ (obs. by Smith).	$K_1 \times 10^5 \text{ sec}^{-1} \text{ (cal.)}$
552.3	6.09	5.75
572.3	27.1	29.2
593.1	132.1	135.1
602.4	274.2	267.6

Attention should also be directed to the recent experimental investigations by Hunt and Daniel ('J. Am. Chem. Soc.', vol. 47, p. 1 (1925)) and Hirst and Rideal ('Roy. Soc. Proc.,' A., vol. 109, p. 526, 1925), on the thermal decomposition of nitrogen pentoxide at low pressures. Their measurements show that the decomposition of  $\text{N}_2\text{O}_5$  has the usual uni-molecular velocity constant even at very low pressures. Furthermore, Hunt and Daniel have been able to demonstrate that this reaction is not autocatalytic as suggested by Rice ('J. Am. Chem. Soc.', vol. 46, p. 2405 (1925)), and that the addition of a large excess of nitrogen does not alter the specific rates of decomposition of  $\text{N}_2\text{O}_5$ . These demonstrations, I believe, prove conclusively that molecular collisions can have no rôle in reactions of this type.]

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*Quantum Mechanics and a Preliminary Investigation of the  
Hydrogen Atom.*

By P. A. M. DIRAC, 1851 Exhibition Senior Research Student, St. John's  
College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received January 22, 1926.)

§ 1. *The Algebraic Laws governing Dynamical Variables.*

Although the classical electrodynamic theory meets with a considerable amount of success in the description of many atomic phenomena, it fails completely on certain fundamental points. It has long been thought that the way out of this difficulty lies in the fact that there is one basic assumption of the classical theory which is false, and that if this assumption were removed and replaced by something more general, the whole of atomic theory would follow quite naturally. Until quite recently, however, one has had no idea of what this assumption could be.

A recent paper by Heisenberg\* provides the clue to the solution of this question, and forms the basis of a new quantum theory. According to Heisenberg, if  $x$  and  $y$  are two functions of the co-ordinates and momenta of a dynamical system, then in general  $xy$  is not equal to  $yx$ . Instead of the commutative law of multiplication, the canonical variables  $q_r, p_r$  ( $r = 1 \dots u$ ) of a system of  $u$  degrees of freedom satisfy the quantum conditions, which were given by the author† in the form

$$\left. \begin{aligned} q_s q_r - q_r q_s &= 0 \\ p_r p_s - p_s p_r &= 0 \\ q_r p_s - p_s q_r &= 0 \\ q_r p_r - p_r q_r &= i\hbar \end{aligned} \right\} \quad (r \neq s) \quad (1)$$

where  $i$  is a root of  $-1$  and  $\hbar$  is a real universal constant, equal to  $(2\pi)^{-1}$  times the usual Planck's constant. These equations are just sufficient to enable one to calculate  $xy - yx$  when  $x$  and  $y$  are given functions of the  $p$ 's and  $q$ 's, and are therefore capable of replacing the classical commutative law of multiplication. They appear to be the simplest assumptions one could make which would give a workable theory.

\* 'Zeits. f. Phys.,' vol. 33, p. 879 (1925).

† 'Roy. Soc. Proc.,' A, vol. 109, p. 642 (1925). These quantum conditions have been obtained independently by Born, Heisenberg and Jordan, 'Zeit. f. Phys.,' vol. 35, p. 557 (1926).



The fact that the variables used for describing a dynamical system do not satisfy the commutative law means, of course, that they are not numbers in the sense of the word previously used in mathematics. To distinguish the two kinds of numbers, we shall call the quantum variables *q*-numbers and the numbers of classical mathematics which satisfy the commutative law *c*-numbers, while the word number alone will be used to denote either a *q*-number or a *c*-number. When  $xy = yx$  we shall say that  $x$  commutes with  $y$ .

At present one can form no picture of what a *q*-number is like. One cannot say that one *q*-number is greater or less than another. All one knows about *q*-numbers is that if  $z_1$  and  $z_2$  are two *q*-numbers, or one *q*-number and one *c*-number, there exist the numbers  $z_1 + z_2$ ,  $z_1 z_2$ ,  $z_2 z_1$ , which will in general be *q*-numbers but may be *c*-numbers. One knows nothing of the processes by which the numbers are formed except that they satisfy all the ordinary laws of algebra, excluding the commutative law of multiplication, i.e.,

$$z_1 + z_2 = z_2 + z_1,$$

$$(z_1 + z_2) + z_3 = z_1 + (z_2 + z_3),$$

$$(z_1 z_2) z_3 = z_1 (z_2 z_3),$$

$$z_1 (z_2 + z_3) = z_1 z_2 + z_1 z_3, \quad (z_1 + z_2) z_3 = z_1 z_3 + z_2 z_3,$$

and if

$$z_1 z_2 = 0,$$

either

$$z_1 = 0 \quad \text{or} \quad z_2 = 0;$$

but

$$z_1 z_2 \neq z_2 z_1,$$

in general, except when  $z_1$  or  $z_2$  is a *c*-number. One may define further numbers,  $x$  say, by means of equations involving  $x$  and the  $z$ 's, such as  $x^2 = z$ , which defines  $z^{\frac{1}{2}}$ , or  $zx = 1$ , which defines  $z^{-1}$ . There may be more than one value of  $x$  satisfying such an equation, but this is not so for the equation  $zx = 1$ , since if  $x_1 z = 1$  and  $x_2 z = 1$  then  $(x_1 - x_2)z = 0$ , which gives  $x_1 = x_2$  provided  $z \neq 0$ .

A function  $f(z)$  of a *q*-number  $z$  cannot be defined in a manner analogous to the general definition of a function of a real *c*-number variable, but can be defined only by an algebraic relation connecting  $f(z)$  with  $(z)$ . When this relation does not involve any *q*-number that does not commute with  $z$  and  $f(z)$ , one can define  $\partial f / \partial z$  without ambiguity by the same algebraic relation as when  $z$  is a *c*-number, e.g., if  $f(z) = z^n$ , then  $\partial f / \partial z = n z^{n-1}$  where  $n$  is a *c*-number.

In order to be able to get results comparable with experiment from our theory, we must have some way of representing q-numbers by means of c-numbers, so that we can compare these c-numbers with experimental values. The representation must satisfy the condition that one can calculate the c-numbers that represent  $x + y$ ,  $xy$ , and  $yx$  when one is given the c-numbers that represent  $x$  and  $y$ . If a q-number  $x$  is a function of the co-ordinates and momenta of a multiply periodic system, and if it is itself multiply periodic, then it will be shown that the aggregate of all its values for all values of the action variables of the system can be represented by a set of harmonic components of the type  $x(nm) \cdot \exp. i \omega(nm)t$ , where  $x(nm)$  and  $\omega(nm)$  are c-numbers, each associated with two sets of values of the action variables denoted by the labels  $n$  and  $m$ , and  $t$  is the time, also a c-number. This representation was taken as defining a q-number in the previous papers on the new theory.\* It seems preferable though to take the above algebraic laws and the general conditions (1) as defining the properties of q-numbers, and to deduce from them that a q-number can be represented by c-numbers in this manner when it has the necessary periodic properties. A q-number thus still has a meaning and can be used in the analysis when it is not multiply periodic, although there is at present no way of representing it by c-numbers.

## § 2. *The Poisson Bracket Expressions.*

If  $x$  and  $y$  are two numbers, we define their Poisson bracket expression  $[x, y]$  by

$$xy - yx = i\hbar [x, y]. \quad (2)$$

It has the following properties, which follow at once from the definition and make it analogous to the Poisson bracket of classical mechanics.

(i) It contains no reference to any particular set of canonical variables.

(ii) It satisfies the laws

$$\begin{aligned} [x_1 + x_2, y] &= [x_1, y] + [x_2, y], \\ [x_1 x_2, y] &= x_1 [x_2, y] + [x_1, y] x_2, \\ [x, y] &= -[y, x]. \end{aligned}$$

(iii) It satisfies the identity

$$[[x, y], z] + [[y, z], x] + [[z, x], y] = 0.$$

\* See particularly, Born and Jordan, 'Zeits. f. Phys.,' vol. 34, p. 858 (1925). Also Born, Heisenberg and Jordan, *loc. cit.*

(iv) The elementary P.B.'s (Poisson brackets) are given, from (1), by

$$[p_r, p_s] = 0, \quad [q_r, q_s] = 0,$$

$$[q_r, p_s] = 0 \quad (r \neq s), \quad \text{or} \quad 1 \quad (r = s),$$

and also

$$[p_r, c] = [q_r, c] = 0,$$

when  $c$  is a c-number.

If  $x$  and  $y$  are given functions of the  $p$ 's and  $q$ 's, then, by successive applications of the laws (ii) the P.B.  $[x, y]$  can be expressed in terms of the elementary P.B.'s occurring in (iv), and thus evaluated. It is often more convenient to evaluate a P.B. in this way than by the direct use of (2). For example, to evaluate  $[q^2, p^2]$  we have

$$[q^2, p^2] = q [q, p^2] + [q, p^2] q,$$

and

$$[q, p^2] = p [q, p] + [q, p] p = 2p,$$

so that

$$[q^2, p^2] = 2qp + 2pq.$$

One may greatly reduce the labour of evaluating P.B.'s of functions of the  $p$ 's and  $q$ 's in certain special cases by observing that the classical theory expression for the P.B.  $[x, y]$ , namely  $\Sigma_r \left( \frac{\partial x}{\partial q_r} \frac{\partial y}{\partial p_r} - \frac{\partial y}{\partial q_r} \frac{\partial x}{\partial p_r} \right)$ , may usually be taken over directly into the quantum theory when this does not give rise to any ambiguity concerning order of factors of products, *e.g.*, we can say at once that

$$[f(x), x] = 0,$$

when  $f(x)$  does not involve any number that does not commute with  $x$ , and also

$$[f(q_r), p_r] = \partial f / \partial q_r, \quad (3)$$

when  $f(q_r)$  does not involve any number that does not commute with  $q_r$ .

The conditions that a set of variable  $Q_r, P_r$  shall be canonical are defined to be that from the relations connecting the  $Q_r, P_r$  with the  $q_r, p_r$  (which are given to be canonical) one can deduce the equations

$$[Q_r, Q_s] = 0, \quad [P_r, P_s] = 0,$$

$$[Q_r, P_s] = 0 \quad (r \neq s) \quad \text{or} \quad 1 \quad (r = s).$$

One could evaluate the P.B. of two functions of the  $Q_r, P_r$  either by working entirely in the variables  $Q_r, P_r$ , or by first substituting for these variables in terms of the  $q_r, p_r$ . The relations connecting the  $Q_r, P_r$  with the  $q_r, p_r$  may be put in the form

$$Q_r = bq_r b^{-1}, \quad P_r = bp_r b^{-1},$$

where  $b$  is a  $q$ -number which determines the transformation, but these formulæ do not appear to be of great practical value.

A dynamical system is determined on the classical theory by a Hamiltonian  $H$ , which is a certain function of the  $p$ 's and  $q$ 's, and the classical equations of motion may be written

$$\dot{x} = [x, H]. \quad (4)$$

We assume that the equations of motion on the quantum theory are also of the form (4), where the Hamiltonian  $H$  is now a  $q$ -number, and is for the present an unknown function of the  $p$ 's and  $q$ 's. The representation of a  $q$ -number by  $c$ -numbers when it is multiply periodic must be such that if  $x$  is represented by the harmonic components  $x(nm) \exp. i\omega(nm)t$ ,  $\dot{x}$  defined by (4) has the components  $i\omega(nm) x(nm) \exp. i\omega(nm)t$ .

### § 3. *Some Elementary Algebraic Theorems.*

In all previous descriptions of natural phenomena the two roots of  $-1$  have always played symmetrical parts. The occurrence of a root of  $-1$  in the fundamental equations (1) means that this is not so in the present theory. For mathematical convenience we shall continually be using in the analysis a root of  $-1$ ,  $j$  say, which is independent of the  $i$  in (1), that is to say, from any equation one can obtain another equation by writing  $-j$  for  $j$  without at the same time changing the sign of  $i$ . From these two equations one can obtain two more equations by reversing the order of the factors of all products occurring in them and at the same time writing  $-h$  for  $h$ , since if this operation is applied to equations (1) it will give correct results, so that it must still give correct results when applied to any equation derivable from (1). To avoid having two symbols  $i$  and  $j$ , both denoting roots of  $-1$ , we shall take  $j = i$ , and must then modify the above rules to read:—From any equation one may obtain another equation by writing  $-i$  for  $i$  wherever it occurs and at the same time writing  $-h$  for  $h$ , or by reversing the order of all factors and writing  $-h$  for  $h$ , or by applying the two previous operations together, which reduces to reversing the order of all factors and writing  $-i$  for  $i$ . This third operation applied to any number gives what may be defined as the conjugate imaginary number. A number is defined to be real if it is equal to its conjugate imaginary.

The remainder of this section will be devoted to some simple analytical rules which will be of use in the subsequent work.

When forming the reciprocal of a quantity composed of two or more factors, one must reverse their order, i.e.,

$$\frac{1}{(xy)} = \frac{1}{y} \cdot \frac{1}{x}. \quad (5)$$

This equation may be verified by multiplying each side by  $xy$  either in front or behind.

To differentiate the reciprocal of a quantity  $x$  one must proceed as follows :—

$$\begin{aligned} \frac{d}{dt} \left( \frac{1}{x} \cdot x \right) &= \frac{d}{dt} (1) = [1, H] = 0. \\ 0 &= \frac{d}{dt} \left( \frac{1}{x} \cdot x \right) = \frac{d}{dt} \left( \frac{1}{x} \right) \cdot x + \frac{1}{x} \dot{x}. \end{aligned}$$

Hence, dividing by  $x$  behind, one gets

$$\frac{d}{dt} \left( \frac{1}{x} \right) = -\frac{1}{x} \dot{x} \frac{1}{x}.$$

The binomial expansion for  $(1+x)^n$  when  $n$  is a c-number is the same as in ordinary algebra. Also one defines  $e^x$  by the same power series as in ordinary algebra. The ordinary exponential law, however, is not valid, i.e.,  $e^{x+y}$  is not in general equal to  $e^x e^y$ , except when  $x$  commutes with  $y$ .

If  $(\alpha q)$  denotes  $\Sigma_r (\alpha_r q_r)$ , where the  $\alpha_r$  ( $r = 1 \dots u$ ) are c-numbers, then from (3)

$$[e^{i(\alpha q)}, p_r] = i\alpha_r e^{i(\alpha q)}.$$

Hence, since

$$e^{i(\alpha q)} p_r - p_r e^{i(\alpha q)} = i\hbar [e^{i(\alpha q)}, p_r],$$

we have

$$e^{i(\alpha q)} p_r = (p_r - \alpha_r \hbar) e^{i(\alpha q)}.$$

More generally, if  $f(q_r, p_r)$  is any function of the  $q$ 's and  $p$ 's,

$$\left. \begin{aligned} e^{i(\alpha q)} f(q_r, p_r) &= f(q_r, p_r - \alpha_r \hbar) e^{i(\alpha q)}, \\ f(q_r, p_r) e^{i(\alpha q)} &= e^{i(\alpha q)} f(q_r, p_r + \alpha_r \hbar). \end{aligned} \right\} \quad (6)$$

To prove this result, we observe that if it is true for any two functions  $f, f_1$  and  $f_2$ , say, it must also be true for  $(f_1 + f_2)$  and  $f_1 f_2$ . Now we have proved it true when  $f = p_r$ , and it is obviously true when  $f = q_r$  since the  $q$ 's commute with each other. Hence it is true when  $f$  is any power series in the  $p$ 's and  $q$ 's so that we may take it to be generally true.

Equations (6) show the law of interchange of any function of the  $p$ 's and  $q$ 's with a quantity of the form  $e^{i(\alpha q)}$ . They are of great value in the theory of multiply periodic systems. There are, of course, corresponding equations for any set of canonical variables,  $Q_r, P_r$ .

§ 4. Multiply Periodic Systems.

A dynamical system is multiply periodic on the quantum theory when there exists a set of uniformising variables  $J_r, w_r$  having the following properties:—

(i) They are canonical variables, i.e.,

$$\begin{aligned} [J_r, J_s] &= 0, & [w_r, w_s] &= 0, \\ [w_r, J_s] &= 0 \quad (r \neq s), \text{ or } 1 \quad (r = s). \end{aligned}$$

(ii) The Hamiltonian  $H$  is a function of the  $J$ 's only.\*

(iii) The original  $p$ 's and  $q$ 's that describe the system are multiply periodic functions of the  $w$ 's of period  $2\pi$ , the condition for this being defined to be that a  $p$  or  $q$  can be expanded in either of the forms

$$\sum_a C_a \exp i (\alpha_1 w_1 + \alpha_2 w_2 + \dots + \alpha_u w_u) = \sum_a C_a \exp i (\alpha w)$$

or

$$\sum_a \exp i (\alpha_1 w_1 + \alpha_2 w_2 + \dots + \alpha_u w_u) C'_a = \sum_a \exp i (\alpha w) C'_a.$$

$C'_a$ , where the  $C_a$ 's and  $C'_a$ 's are functions of the  $J$ 's only and the  $\alpha$ 's are integers. We have taken the  $w$ 's  $2\pi$  times as great and the  $J$ 's  $1/2\pi$  times as great as the usual uniformising variables in order to save writing.

We have at once

$$\dot{J}_r = [J_r, H] = 0$$

from (ii), and

$$\dot{w}_r = [w_r, H] = \partial H / \partial J_r,$$

using (3). The quantities  $\dot{w}_r$  are, therefore, constants and may be called the frequencies. There are, however, other quantities that have claims to be called frequencies. We have

$$\frac{d}{dt} e^{i(\alpha w)} = [e^{i(\alpha w)}, H] = \frac{e^{i(\alpha w)} H - H e^{i(\alpha w)}}{i\hbar}.$$

From (6) applied to the  $J$ 's and  $w$ 's,

$$e^{i(\alpha w)} H(J_r) = H(J_r - \alpha_r \hbar) e^{i(\alpha w)},$$

and

$$H(J_r) e^{i(\alpha w)} = e^{i(\alpha w)} H(J_r + \alpha_r \hbar).$$

Hence

$$\frac{d}{dt} e^{i(\alpha w)} = i(\alpha \omega) e^{i(\alpha w)} = i e^{i(\alpha w)} (\alpha \omega)',$$

where

$$\left. \begin{aligned} (\alpha \omega) \hbar &= H(J_r) - H(J_r - \alpha_r \hbar), \\ (\alpha \omega)' \hbar &= H(J_r + \alpha_r \hbar) - H(J_r), \end{aligned} \right\} \quad (7)$$

\* He is not necessarily the same function of the  $J$ 's as on the classical theory with the present definition of the  $J$ 's.

The quantities  $\dot{w}_r$  correspond to the orbital frequencies on Bohr's theory, while the  $(\alpha\omega)$  and  $(\alpha\omega)'$  correspond, when the  $\alpha$ 's are integers, to the transition frequencies. It must be remembered though that the  $w_r$ ,  $(\alpha\omega)$  and  $(\alpha\omega)'$  are q-numbers, and, therefore, they cannot be equated to Bohr's frequencies, which are c-numbers. They are merely the same functions of the present J's, which are q-numbers, as Bohr's frequencies are of his J's, which are c-numbers.

Suppose  $x$  can be expanded in the form

$$x = \sum_a x_a e^{i(\alpha\omega)} = \sum_a e^{i(\alpha\omega)} x_a', \quad (8)$$

where the  $\alpha$ 's are integers and the  $x_a, x_a'$  are functions of the J's only. From (6)

$$x_a' (J_r) = x_a (J_r + \alpha_r h).$$

Also

$$x = \sum_a x_a i(\alpha\omega) e^{i(\alpha\omega)} = \sum_a e^{i(\alpha\omega)} i(\alpha\omega)' x_a' \quad (9)$$

If  $x$  and the J's are real and if  $\bar{x}_a$  denotes the conjugate imaginary of  $x_a$ , then by equating the conjugate imaginaries of both sides of (8) we get

$$x = \sum_a e^{-i(\alpha\omega)} \bar{x}_a (J_r) = \sum_a \bar{x}_a (J_r + \alpha_r h) e^{-i(\alpha\omega)}.$$

Comparing this with equation (8) we find that

$$\bar{x}_a (J_r + \alpha_r h) = x_{-a} (J_r).$$

This relation is brought out more clearly if we change the notation. For  $x_a (J_r)$  write  $x (J, J - \alpha h)$ .

Then

$$\bar{x} (J + \alpha h, J) = x (J, J + \alpha h),$$

which shows that there is some kind of symmetry in the way in which the amplitude  $x (J, J - \alpha h)$  is related to the two sets of variables to which it explicitly refers. Our expansion for  $x$  is now

$$x = \sum_a x (J, J - \alpha h) e^{i(\alpha\omega)} = \sum_a e^{i(\alpha\omega)} x (J + \alpha h, J).$$

The expressions (7) for the transition frequencies suggest that we should put

$$(\alpha\omega) (J) = \omega (J, J - \alpha h),$$

and

$$(\alpha\omega)' (J) = \omega (J + \alpha h, J).$$

We should then have from (9)

$$x = \sum x (J, J - \alpha h) i\omega (J, J - \alpha h) e^{i(\alpha\omega)} = \sum e^{i(\alpha\omega)} i\omega (J + \alpha h, J) x (J + \alpha h, J). \quad (10)$$

Suppose  $y$  can also be expanded in the form

$$y = \sum_{\beta} y(J, J - \beta h) e^{i(\beta w)}.$$

Then

$$\begin{aligned} xy &= \sum_{\alpha\beta} x(J, J - \alpha h) e^{i(\alpha w)} y(J, J - \beta h) e^{i(\beta w)}, \\ &= \sum_{\alpha\beta} x(J, J - \alpha h) \cdot y(J - \alpha h, J - \alpha h - \beta h) e^{i[(\alpha+\beta)w]}, \end{aligned}$$

by again using (6), and the fact that the  $w$ 's commute; or, the amplitudes of  $xy$  are given by

$$xy(J, J - \gamma h) = \sum_{\alpha} x(J, J - \alpha h) \cdot y(J - \alpha h, J - \gamma h). \quad (11)$$

These formulæ provide a way of representing  $q$ -numbers by means of  $c$ -numbers. Suppose that in the expressions  $x(J, J - \alpha h)$  and  $\omega(J, J - \alpha h)$ , considered merely as functions of the  $J$ 's, we substitute for each  $J_r$  the  $c$ -number  $n_r h$ , and denote the resulting  $c$ -numbers by  $x(n, n - \alpha)$  and  $\omega(n, n - \alpha)$ . We may consider the aggregate of all the  $c$ -numbers  $x(n, n - \alpha) \exp. i\omega(n, n - \alpha)t$ , in which it is sufficient (but not necessary) for the  $n$  to take a series of values differing successively by unity, as representing the values of the  $q$ -number  $x$  for all values of the  $q$ -numbers  $J_r$ . Equation (10) shows that

$$\dot{x}(n, n - \alpha) = i\omega(n, n - \alpha) x(n, n - \alpha),$$

while equation (11) gives

$$xy(n, n - \gamma) = \sum_{\alpha} x(n, n - \alpha) y(n - \alpha, n - \gamma),$$

which is just Heisenberg's law of multiplication. Also we have obviously

$$(x + y)(n, n - \alpha) = x(n, n - \alpha) + y(n, n - \alpha).$$

Our representation thus satisfies the conditions mentioned in §§ 1 and 2, which proves the sufficiency of this discrete set of  $n$ 's.

One gets different representations of the  $q$ -numbers  $x$  by  $c$ -numbers  $x(n, m)$   $\exp. i\omega(n, m)t$  by taking different values for the  $c$ -numbers,  $n_r$ , say, by which the  $n_r$ 's differ from integers. Only one of these representations, though, is of physical importance, this being the one (assumed to exist) for which, every  $x(n, m)$  vanishes when an  $m_r$  is less than a certain value,  $n_{or}$ , say, which fixes the normal state of the system on Bohr's theory, and each  $n_r \geq n_{or}$ . This requires that every coefficient  $x(J, J - \alpha h)$  in the expansion of  $x$  shall vanish when for each  $J_r$  is substituted the  $c$ -number  $(n_{or} + m_r h)$ , where the  $m_r$  are integers not less than zero, at least one of which is less than the corresponding  $\alpha_r$ .



§ 5. *Orbital Motion in the Hydrogen Atom.*

It is necessary at this point to make some assumption of the form of the Hamiltonian for the hydrogen atom.\* We may assume that it is the same function of the Cartesian co-ordinates  $x, y$  and their corresponding momenta  $p_x, p_y$  as on the classical theory, i.e.,

$$H = \frac{1}{2m} (p_x^2 + p_y^2) - \frac{e^2}{(x^2 + y^2)^{\frac{1}{2}}},$$

where  $e$  and  $m$  are c-numbers.

We transform to polar co-ordinates  $r, \theta$  by means of the equations

$$x = r \cos \theta, \quad y = r \sin \theta,$$

where  $\cos \theta$  and  $\sin \theta$  are defined in terms of  $e^{i\theta}$  by the same relations as on the classical theory. The momenta  $p_r$  and  $k$  conjugate to  $r$  and  $\theta$  are given by the equations

$$p_r = \frac{1}{2} (p_x \cos \theta + \cos \theta p_x) + \frac{1}{2} (p_y \sin \theta + \sin \theta p_y)$$

$$k = xp_y - yp_x.$$

To verify that  $r, \theta, p_r, k$  defined in this way are canonical variables, we must work out all their P.B.'s taken two at a time. We have at once that  $x, y, r$  and  $\theta$  commute with one another. Also

$$[r, p_x] = [(x^2 + y^2)^{\frac{1}{2}}, p_x] = x/(x^2 + y^2)^{\frac{1}{2}} = \cos \theta,$$

with the help of (3), and similarly

$$[r, p_y] = \sin \theta,$$

so that

$$\begin{aligned} [r, k] &= x[r, p_y] - y[r, p_x] \\ &= x \sin \theta - y \cos \theta = 0, \end{aligned}$$

and

$$\begin{aligned} [r, p_r] &= \frac{1}{2} [r, p_x] \cos \theta + \frac{1}{2} \cos \theta [r, p_x] + \frac{1}{2} [r, p_y] \sin \theta + \frac{1}{2} \sin \theta [r, p_y] \\ &= \cos^2 \theta + \sin^2 \theta = 1. \end{aligned}$$

Further

$$\begin{aligned} r[e^{i\theta}, k] &= [re^{i\theta}, k] = [x + iy, xp_y - yp_x] \\ &= ix[y, p_y] - y[x, p_x] = ix - y = i r e^{i\theta}, \end{aligned}$$

so that

$$[e^{i\theta}, k] = i e^{i\theta}.$$

\* The hydrogen atom has been treated on the new mechanics by Pauli in a paper not yet published.

The remaining equations,  $[e^{i\theta}, p_r] = 0$  and  $[k, p_r] = 0$ , may be likewise verified by elementary quantum algebra.

If we solve for  $p_x, p_y$  in terms of  $p_r, k$ , we find that

$$\begin{aligned} p_x + i p_y &= (p_r + i k_2/r) e^{i\theta} = e^{i\theta} (p_r + i k_1/r), \\ p_x - i p_y &= (p_r - i k_1/r) e^{-i\theta} = e^{-i\theta} (p_r - i k_2/r), \end{aligned}$$

where

$$k_1 = k + \frac{1}{2} h, \quad k_2 = k - \frac{1}{2} h,$$

so that

$$k_2 e^{i\theta} = e^{i\theta} k_1, \quad k_1 e^{-i\theta} = e^{-i\theta} k_2$$

by an application of (6). We thus have

$$\begin{aligned} p_x^2 + p_y^2 &= (p_x - i p_y)(p_x + i p_y) = (p_r - i k_1/r)(p_r + i k_1/r), \\ &= p_r^2 + \frac{k_1^2}{r^2} + i k_1 (p_r \frac{1}{r} - \frac{1}{r} p_r), \end{aligned} \quad (12)$$

Now

$$p_r \frac{1}{r} - \frac{1}{r} p_r = \frac{1}{r} (r p_r - p_r r) \frac{1}{r} = \frac{i\hbar}{r^2}.$$

Hence

$$p_x^2 + p_y^2 = p_r^2 + \frac{k_1^2 - k_1 h}{r^2} = p_r^2 + \frac{k_1 k_2}{r^2},$$

and

$$H = \frac{1}{2m} \left( p_r^2 + \frac{k_1 k_2}{r^2} \right) - \frac{e^2}{r}. \quad (13)$$

If we had originally assumed that the Hamiltonian was the same function of the polar variables as on the classical theory, we should have had instead

$$H = \frac{1}{2m} \left( p_r^2 + \frac{k^2}{r^2} \right) - \frac{e^2}{r}. \quad (13')$$

The only way to decide which of these assumptions is correct is to work out the consequences of both and to see which agrees with experiment.

The equations of motion with either Hamiltonian are

$$\begin{aligned} \dot{r} &= [r, H] = p_r/m, \\ k &= [k, H] = 0, \\ \dot{\theta} &= [\theta, H] = k/mr^2, \end{aligned}$$

which give  $p_r = m\dot{r}$ ,  $k = \text{constant}$  and  $mr^2\dot{\theta} = k$ , as on the classical theory, and finally

$$p_r = [p_r, H] = \frac{k_1 k_2}{mr^3} - \frac{e^2}{r^2} \quad \text{with (13)} \quad (14)$$

$$= \frac{k^2}{mr^3} - \frac{e^2}{r^2} \quad \text{with (13')} \quad (14')$$

We try to find an integral of the equations of motion of the form

$$1/r = a_0 + a_1 e^{i\theta} + a_2 e^{-i\theta}, \quad (15)$$

where  $a_0$ ,  $a_1$  and  $a_2$  are constants, corresponding to the classical equation of elliptic motion

$$l/r = 1 + \varepsilon \cos(\theta - \alpha)$$

in which  $l$  is the latus rectum and  $\varepsilon$  the excentricity.

The rate of change of  $e^{i\theta}$  is given with either  $H$  by

$$\begin{aligned} \frac{d}{dt} e^{i\theta} &= [e^{i\theta}, H] = [e^{i\theta}, k^2] \frac{1}{2mr^2}, \\ &= \{k[e^{i\theta}, k] + [e^{i\theta}, k]k\}/2mr^2, \\ &= \{kie^{i\theta} + ie^{i\theta}k\}/2mr^2, \\ &= \frac{i}{m} e^{i\theta} \frac{k_1}{r^2} = \frac{i}{m} \frac{k_2}{r^2} e^{i\theta}. \end{aligned}$$

By changing the sign of both  $i$  and  $h$  we find

$$\frac{d}{dt} e^{-i\theta} = -\frac{i}{m} e^{-i\theta} \frac{k_2}{r^2} = -\frac{i}{m} \frac{k_1}{r^2} e^{-i\theta}.$$

Hence if we differentiate (15) we get

$$-\frac{1}{r} \dot{r} \frac{1}{r} = \frac{i}{m} (a_1 e^{i\theta} k_1 - a_2 e^{-i\theta} k_2) \frac{1}{r^2},$$

or

$$1/r \cdot p_r r = -i(a_1 e^{i\theta} k_1 - a_2 e^{-i\theta} k_2),$$

which, using

$$p_r = 1/r \cdot p_r r = ih/r,$$

reduces to

$$\begin{aligned} p_r &= -i(a_1 e^{i\theta} k_1 - a_2 e^{-i\theta} k_2) + ih/r, \\ &= -i(a_1 e^{i\theta} k_1 - a_2 e^{-i\theta} k_2) + ih(a_0 + a_1 e^{i\theta} + a_2 e^{-i\theta}), \\ &= i(a_0 h - a_1 e^{i\theta} k_2 + a_2 e^{-i\theta} k_1). \end{aligned} \quad (16)$$

Now differentiate again. The result is

$$\begin{aligned} m\dot{p}_r &= a_1 e^{i\theta} k_1 k_2 / r^2 + a_2 e^{-i\theta} k_2 k_1 / r^2 \\ &= \left(\frac{1}{r} - a_0\right) \frac{k_1 k_2}{r^2} = \frac{k_1 k_2}{r^3} - \frac{a_0 k_1 k_2}{r^2}, \end{aligned}$$

which agrees with the equation of motion (14) if one takes  $a_0 = me^2/k_1 k_2$ , but will not agree with (14').

We can easily obtain an integral of (14') by making a small change in (15). We transform from the variables  $r, \theta, p_r, k$  to the variables  $r, \theta', p_r, k'$ , where

$$k' = (k^2 + \frac{1}{4}h^2)^{\frac{1}{2}}, \theta' = \theta + k'/k,$$

which are canonical since

$$[\theta', k'] = [\theta, k'] \frac{k'}{k} = \frac{k}{(k^2 + \frac{1}{4}h^2)^{\frac{1}{2}}} \frac{k'}{k} = 1,$$

and take

$$1/r = a_0 + a_1 e^{i\theta'} + a_2 e^{-i\theta'}. \quad (15')$$

Proceeding exactly as before, we find that

$$\frac{d}{dt} e^{i\theta'} = \frac{i}{m} e^{i\theta'} \frac{k_1'}{r^2}, \quad \frac{d}{dt} e^{-i\theta'} = -\frac{i}{m} e^{-i\theta'} \frac{k_2'}{r^2},$$

where

$$k_1' = k' + \frac{1}{2}h, \quad k_2' = k' - \frac{1}{2}h,$$

and further that

$$m\dot{p}_r = \frac{k_1' k_2'}{r^3} - \frac{a_0 k_1' k_2'}{r^2} = \frac{k^2}{r^3} - \frac{a_0 k^2}{r^2},$$

which agrees with (14') if we take  $a_0 = me^2/k^2$ .

With the Hamiltonian (13') the orbit of the electron is thus an ellipse with a rotating apse line. If the Cartesian co-ordinates are now expanded in multiple Fourier series, two angle variables will be required, which will give two orbital frequencies. There would therefore necessarily be a two-fold infinity of energy-levels, which disagrees with experiment (when one disregards the relativity fine-structure of the hydrogen spectrum). The assumption of the Hamiltonian (13') is thus untenable.

We therefore assume the Hamiltonian (13), which does give a degenerate motion, and proceed to evaluate the frequencies.

### § 6. Determination of the Constants of Integration.

The equation of the orbit is now given by (15), or

$$1/r = me^2/k_1 k_2 + a_1 e^{i\theta} + a_2 e^{-i\theta}, \quad (17)$$

and from (16)

$$p_r = i(me^2 h/k_1 k_2 - a_1 e^{i\theta} k_2 + a_2 e^{-i\theta} k_1). \quad (18)$$

We must determine the form of the constants of integration  $a_1$  and  $a_2$ .

Since  $k$  commutes with  $r$  and  $p_r$ , it follows from (17) and (18) that it commutes with  $(a_1 e^{i\theta} + a_2 e^{-i\theta})$  and  $(a_1 e^{i\theta} k_2 - a_2 e^{-i\theta} k_1)$ . Hence  $k$  must commute with  $a_1 e^{i\theta}$  and  $a_2 e^{-i\theta}$  separately.

From (17) and (18) we find

$$\begin{aligned}\frac{k_1}{r} + ip_r &= \frac{me^2}{k_1 k_2} k_1 + a_1 e^{i\theta} k_1 + a_2 e^{-i\theta} k_1 - \frac{me^2 h}{k_1 k_2} + a_1 e^{i\theta} k_2 - a_2 e^{-i\theta} k_1, \\ &= me^2/k_1 + 2ka_1 e^{i\theta}, \\ &= me^2/k_1 + 2c_1 e^{i\theta},\end{aligned}\quad (19)$$

where  $a_1 = k^{-1}c_1$ . Multiplying this equation by  $e^{i\theta}$  in front and  $e^{-i\theta}$  behind we get, since  $e^{i\theta}f(k_1)e^{-i\theta} = f(k_2)$ ,

$$k_2/r + ip_r = me^2/k_2 + 2e^{i\theta}c_1. \quad (20)$$

Hence

$$c_1 e^{i\theta} - e^{i\theta}c_1 = \frac{1}{2} \frac{k_1 - k_2}{r} - \frac{1}{2} me^2 \left( \frac{1}{k_1} - \frac{1}{k_2} \right) = \frac{1}{2} \frac{h}{r} + \frac{me^2 h}{2k_1 k_2}. \quad (21)$$

Similarly, if  $a_2 = k^{-1}c_2$ , it may be shown that

$$c_2 e^{-i\theta} - e^{-i\theta}c_2 = -\frac{1}{2} \frac{h}{r} - \frac{me^2 h}{2k_1 k_2}, \quad (22)$$

so that

$$c_1 e^{i\theta} + c_2 e^{-i\theta} = e^{i\theta}c_1 + e^{-i\theta}c_2.$$

Hence, as  $k$  commutes with  $c_1 e^{i\theta}$  and  $c_2 e^{-i\theta}$ ,

$$\frac{1}{r} = \frac{me^2}{k_1 k_2} + \frac{1}{k} (c_1 e^{i\theta} + c_2 e^{-i\theta}) = \frac{me^2}{k_1 k_2} + (e^{i\theta}c_1 + e^{-i\theta}c_2) \frac{1}{k}. \quad (23)$$

We could, of course, have obtained directly from the equations of motion an integral of the form

$$1/r = a_0' + e^{i\theta} a_1' + e^{-i\theta} a_2'.$$

Equations (23) show the relations between the  $a$ 's and the  $a$ 's. From (21) and (22) the following two additional forms for  $1/r$  are easily obtained:—

$$\frac{1}{r} = \frac{me^2}{k_1^2} + \frac{1}{k_1} (c_1 e^{i\theta} + e^{-i\theta}c_2) = \frac{me^2}{k_2^2} + \frac{1}{k_2} (e^{i\theta}c_1 + c_2 e^{-i\theta}). \quad (24)$$

The equations

$$k_2/r - ip_r = me^2/k_2 + 2c_2 e^{-i\theta}, \quad (25)$$

and

$$k_1/r - ip_r = me^2/k_1 + 2e^{-i\theta}c_2 \quad (26)$$

may be obtained in the same way in which (19) and (20) were obtained. Multiply corresponding sides of equations (19) and (26), putting (19) first. The left-hand side of the result is

$$\begin{aligned}\left(\frac{k_1}{r} + ip_r\right)\left(\frac{k_2}{r} - ip_r\right) \\ &= k_1 k_2/r^2 + p_r^2, \\ &= 2m(H + e^2/r),\end{aligned}$$

using (12) and (13), while the right-hand side is

$$\frac{m^2 e^4}{k_1^2} + \frac{2me^2}{k_1} (c_1 e^{i\theta} + e^{-i\theta} c_2) + 4c_1 c_2 = \frac{2me^2}{r} - \frac{m^2 e^4}{k_1^2} + 4c_1 c_2,$$

using the first of equations (24). Hence

$$2mH = 4c_1 c_2 - m^2 e^4 / k_1^2.$$

Similarly, by multiplying corresponding sides of equations (20) and (25) taking (25) first, we find that,

$$2mH = 4c_2 c_1 - m^2 e^4 / k_2^2.$$

Put

$$2mH = -m^2 e^4 / P^2.$$

P, of course, commutes with  $k$ ,  $c_1$  and  $c_2$ . We then have

$$\left. \begin{aligned} c_1 c_2 &= \frac{1}{4} m^2 e^4 \left( \frac{1}{k_1^2} - \frac{1}{P^2} \right) = \frac{1}{4} m^2 e^4 \frac{\epsilon_1^2}{k_1^2}, \\ c_2 c_1 &= \frac{1}{4} m^2 e^4 \left( \frac{1}{k_2^2} - \frac{1}{P^2} \right) = \frac{1}{4} m^2 e^4 \frac{\epsilon_2^2}{k_2^2}, \end{aligned} \right\} (27)$$

where

$$\epsilon_1 = \sqrt{1 - \frac{k_1^2}{P^2}}, \quad \epsilon_2 = \sqrt{1 - \frac{k_2^2}{P^2}}.$$

The excentricities  $\epsilon_1$  and  $\epsilon_2$  are constants, and commute with P and  $k$  and with each other.

Put

$$c_1 = \frac{1}{2} m e^2 \epsilon_1 / k_1 \cdot e^{-i\chi}.$$

$\chi$  is a constant and so commutes with P. Since  $k$  commutes with  $c_1 e^{i\theta}$  and with  $\epsilon_1 / k_1$ , it must commute with  $e^{-i\chi} e^{i\theta}$ , so that

$$k e^{-i\chi} e^{i\theta} = e^{-i\chi} e^{i\theta} k = e^{-i\chi} (k - h) e^{i\theta}.$$

Hence

$$k e^{-i\chi} = e^{-i\chi} (k - h).$$

This law for the interchange of  $e^{-i\chi}$  and  $k$  shows that  $\chi$  is canonically conjugate to  $k$ .  $\chi$  corresponds on the classical theory to the angle between the major axis of the ellipse and the line  $\theta = 0$ . We now have

$$c_1 = \frac{1}{2} m e^2 \epsilon_1 / k_1 \cdot e^{-i\chi} = \frac{1}{2} m e^2 e^{-i\chi} \epsilon_2 / k_2,$$

and from (27)

$$c_2 = \frac{1}{2} m e^2 e^{i\chi} \epsilon_1 / k_1 = \frac{1}{2} m e^2 \epsilon_2 / k_2 \cdot e^{i\chi}.$$

The expression (17) for  $1/r$  thus takes the form

$$\frac{1}{r} = \frac{m e^2}{k_1 k_2} \left\{ 1 + \frac{1}{2} \frac{k_2}{k} \epsilon_1 e^{-i\chi} e^{i\theta} + \frac{1}{2} \frac{k_1}{k} \epsilon_2 e^{i\chi} e^{-i\theta} \right\}. \quad (28)$$

§ 7. *Calculation of the Frequencies.*

The easiest frequency to determine is the orbital one  $\dot{w}$ , whose evaluation closely follows the classical calculation of the period. The relation between  $\theta$  and the angle variable  $w$  is of the form

$$\theta = w + \sum b_n e^{niw} = w + \sum b_n' e^{ni\theta},$$

where the  $b$ 's are constants. On differentiating, this gives

$$\dot{\theta} = \dot{w} + \sum' b_n' \frac{ni}{m} (k - \frac{1}{2}nh) e^{ni\theta} \frac{1}{r^2}.$$

Where  $\sum'$  denotes that the term corresponding to  $n = 0$  is omitted from the summation. Multiplying both sides by  $r^2$  behind, we get

$$\dot{\theta} r^2 = \dot{w} r^2 + \sum' b_n'' e^{ni\theta},$$

which gives, since  $mr^2\dot{\theta} = k$ ,

$$r^2 = \frac{k}{m\dot{w}} - \sum' \frac{1}{\dot{w}} b_n'' e^{ni\theta}.$$

Hence if  $r^2$  is expanded as a Fourier series in  $\theta$  with each of the factors  $e^{ni\theta}$  behind its respective coefficient, the constant term will be  $k/m\dot{w}$ , as on the classical theory.

From (28) we have

$$\begin{aligned} r^2 &= \left\{ \frac{me^2}{k_1 k_2} \left( 1 + \frac{1}{2} \frac{k_2 \epsilon_1}{k} e^{-i\chi} e^{i\theta} + \frac{1}{2} \frac{k_1 \epsilon_2}{k} e^{i\chi} e^{-i\theta} \right) \right\}^{-2}, \\ &= \{ \alpha_0 + \alpha_1 e^{-i\chi} e^{i\theta} + \alpha_2 e^{i\chi} e^{-i\theta} \}^{-2}, \end{aligned}$$

say. We can expand the right-hand side by the binomial theorem. This will give a series of terms containing  $e^{i\theta}$ 's mixed up with  $\alpha$ 's, which cannot easily be evaluated. A more satisfactory way of proceeding is as follows:

It can be shown that  $r^n$  is equal to the expression obtained by expanding  $(\alpha_0 + \alpha_1 e^{-i\chi} + \alpha_2 e^{i\chi})^{-n}$  in powers of  $e^{i\chi}$ , and inserting after each term of the form  $\beta_s e^{si\chi}$ , where  $\beta_s$  is independent of  $\chi$ , the requisite power of  $e^{i\theta}$ , namely  $e^{-si\theta}$ . To prove this theorem we assume it to be true for some value of  $n$ , and deduce from that, that it is true for  $n + 1$ . Suppose for instance that

$$(\alpha_0 + \alpha_1 e^{-i\chi} + \alpha_2 e^{i\chi})^{-n} = \sum \beta_s e^{si\chi}, \quad (29)$$

and

$$r^n = \sum \beta_s e^{si\chi} e^{-si\theta}. \quad (30)$$

Let

$$r^{n+1} = \sum \gamma_s e^{si\chi} e^{-si\theta},$$

then

$$\begin{aligned} r^n &= \sum \gamma_s e^{si\chi} e^{-si\theta} \frac{1}{r} = \sum \gamma_s e^{si\chi} \frac{1}{r} e^{-si\theta}, \\ &= \sum \gamma_s e^{si\chi} (\alpha_0 + \alpha_1 e^{-i\chi} e^{i\theta} + \alpha_2 e^{i\chi} e^{-i\theta}) e^{-si\theta}. \end{aligned}$$

Comparing this with (30), we see that

$$\beta_s e^{s\chi} = \gamma_s e^{s\chi} \alpha_0 + \gamma_{s+1} e^{(s+1)\chi} \alpha_1 e^{-\chi} + \gamma_{s-1} e^{(s-1)\chi} \alpha_2 e^{\chi};$$

but this is just the condition that

$$\Sigma \beta_s e^{s\chi} = \Sigma \gamma_s e^{s\chi} (\alpha_0 + \alpha_1 e^{-\chi} + \alpha_2 e^{\chi}).$$

(Note that a term like  $\gamma_{s+1} e^{(s+1)\chi} \alpha_1 e^{-\chi}$  is equal to something independent of  $\chi$  multiplied by  $e^{s\chi}$ , owing to the special nature of the laws of interchange of the  $\alpha$ 's with the  $e^{\chi}$ 's.) Hence from (29)

$$\Sigma \gamma_s e^{s\chi} = (\alpha_0 + \alpha_1 e^{-\chi} + \alpha_2 e^{\chi})^{-n-1},$$

which proves the theorem.

Our problem thus reduces to the determination of the term independent of  $\chi$  in the expansion of  $(\alpha_0 + \alpha_1 e^{-\chi} + \alpha_2 e^{\chi})^{-2}$ . To do this we first factorise the expression  $(\alpha_0 + \alpha_1 e^{-\chi} + \alpha_2 e^{\chi})$ . We have

$$\begin{aligned} (\alpha_0 + \alpha_1 e^{-\chi} + \alpha_2 e^{\chi}) &= \frac{me^2}{2kk_1} \left( 2 \frac{k}{k_2} + \varepsilon_1 e^{-\chi} + \varepsilon_2 \frac{k_1}{k_2} e^{\chi} \right), \\ &= \frac{me^2}{2kk_1} \left\{ \left( 1 + \frac{k_1}{P} \right) + \frac{k_1}{k_2} \left( 1 - \frac{k_2}{P} \right) \right. \\ &\quad \left. + \varepsilon_1 e^{-\chi} + e^{\chi} \varepsilon_1 \frac{k_1 + h}{k_1} \right\}, \\ &= \frac{me^2}{2kk_1} \left\{ \sqrt{1 + \frac{k_1}{P}} + e^{\chi} \frac{k_1 + h}{k_1} \sqrt{1 - \frac{k_1}{P}} \right\} \\ &\quad \left\{ \sqrt{1 + \frac{k_1}{P}} + \sqrt{1 - \frac{k_1}{P}} e^{-\chi} \right\}, \\ &= \frac{me^2}{2kk_1} \sqrt{1 + \frac{k_1}{P}} \left\{ 1 + \frac{k_1}{k_2} \sqrt{\frac{P - k_2}{P + k_1}} e^{\chi} \right\} \\ &\quad \left\{ 1 + e^{-\chi} \sqrt{\frac{P - k_2}{P + k_1}} \right\} \sqrt{1 + \frac{k_1}{P}}. \end{aligned}$$

We must now express  $(\alpha_0 + \alpha_1 e^{-\chi} + \alpha_2 e^{\chi})^{-1}$  in the form of partial fractions. Putting for brevity  $(P + k_1)^{\frac{1}{2}} = \lambda_1$ ,  $(P + k_2)^{\frac{1}{2}} = \lambda_2$ ,  $(P - k_1)^{\frac{1}{2}} = \mu_1$ ,  $(P - k_2)^{\frac{1}{2}} = \mu_2$ , we have, remembering (5),

$$\begin{aligned} (\alpha_0 + \alpha_1 e^{-\chi} + \alpha_2 e^{\chi})^{-1} &= \frac{2P}{me^2} \cdot \frac{1}{\lambda_1} \cdot \frac{1}{1 + e^{-\chi} \mu_2 / \lambda_1} \cdot \frac{1}{1 + k_1 \mu_2 / k_2 \lambda_1 e^{\chi}} \cdot \frac{kk_1}{\lambda_1}, \\ &= \frac{2P}{me^2} \cdot \frac{1}{\lambda_1} \cdot \frac{1}{e^{\chi} + \mu_2 / \lambda_1} \cdot e^{\chi} \cdot \frac{1}{1 + k_1 \mu_2 / k_2 \lambda_1 \cdot e^{\chi}} \cdot \frac{kk_1}{\lambda_1}. \end{aligned}$$



Now it is easily verified that

$$e^{ix} = \left( e^{ix} + \frac{\mu_2}{\lambda_1} \right) \frac{\lambda_1^2}{2k_1} - \frac{\lambda_1 \mu_2}{2k_1} \left( 1 + \frac{k_1 \mu_2}{k_2 \lambda_1} e^{ix} \right).$$

Hence

$$\begin{aligned} (\alpha_0 + \alpha_1 e^{-ix} + \alpha_2 e^{ix})^{-1} &= \frac{P}{m^2} \frac{\lambda_1}{k_1} \frac{1}{1 + k_1 \mu_2 / k_2 \lambda_1 \cdot e^{ix}} \frac{k k_1}{\lambda_1} \\ &\quad - \frac{P}{m^2} \frac{1}{\lambda_1} \frac{1}{e^{ix} + \mu_2 / \lambda_1} \mu_2 k. \end{aligned} \quad (31)$$

We must now square the expression on the right, which will give four terms, and must expand each of them by the binomial theorem and take out the part independent of  $\chi$ . The term

$$\left[ \frac{P}{m^2} \frac{\lambda_1}{k_1} \frac{1}{1 + k_1 \mu_2 / k_2 \lambda_1 \cdot e^{ix}} \frac{k k_1}{\lambda_1} \right]^2$$

will contribute  $(Pk/m^2)^2$ . The term

$$\left[ \frac{P}{m^2} \frac{1}{\lambda_1} \frac{1}{e^{ix} + \mu_2 / \lambda_1} \mu_2 k \right]^2$$

will contribute nothing, since  $(e^{ix} + \mu_2 / \lambda_1)^{-1} = e^{-ix} (1 + \mu_2 / \lambda_1 \cdot e^{-ix})^{-1}$ , which, when expanded, consists only of terms of the form  $e^{-nix}$  with  $n > 0$ . The remaining two terms may best be evaluated by using partial fractions again. It is easily verified that

$$\begin{aligned} & - \frac{P}{m^2} \frac{\lambda_1}{k_1} \frac{1}{1 + k_1 \mu_2 / k_2 \lambda_1 \cdot e^{ix}} \frac{k k_1}{\lambda_1} \cdot \frac{P}{m^2} \frac{1}{\lambda_1} \frac{1}{e^{ix} + \mu_2 / \lambda_1} \mu_2 k \\ &= - \frac{P^2}{m^2 e^4} \frac{\lambda_1}{k_1} \left\{ \frac{1}{2} k_1 \frac{1}{e^{ix} + \mu_2 / \lambda_1} - \frac{1}{1 + k_1 \mu_2 / k_2 \lambda_1 \cdot e^{ix}} \frac{1}{2} \frac{k_1 \mu_2}{\lambda_1} \right\} \mu_2 k, \end{aligned}$$

and

$$\begin{aligned} & - \frac{P}{m^2} \frac{1}{\lambda_1} \frac{1}{e^{ix} + \mu_2 / \lambda_1} \mu_2 k \cdot \frac{P}{m^2} \frac{\lambda_1}{k_1} \frac{1}{1 + k_1 \mu_2 / k_2 \lambda_1 \cdot e^{ix}} \frac{k k_1}{\lambda_1} \\ &= - \frac{P^2}{m^2 e^4} \frac{1}{\lambda_1} \left\{ - \frac{\lambda_1^2 \mu_1^2}{2 k_1} \frac{1}{1 + k_1 \mu_2 / k_2 \lambda_1 \cdot e^{ix}} + \frac{1}{e^{ix} + \mu_2 / \lambda_1} \frac{\lambda_1 \lambda_2^2 \mu_2}{2 k_1} \right\} \frac{k k_1}{\lambda_1}. \end{aligned}$$

The first of these thus contributes

$$\frac{P^2}{m^2 e^4} \frac{\lambda_1}{k_1} \cdot \frac{1}{2} \frac{k_1 \mu_2}{\lambda_1} \cdot \mu_2 k = \frac{P^2 k}{2 m^2 e^4} (P - k_2),$$

and the second

$$\frac{P^2}{m^2 e^4} \frac{1}{\lambda_1} \cdot \frac{\lambda_1^2 \mu_1^2}{2 k_1} \cdot \frac{k k_1}{\lambda_1} = \frac{P^2 k}{2 m^2 e^4} (P - k_1).$$

We therefore have for the term independent of  $\chi$  in the expansion of  $(\alpha_0 + \alpha_1 e^{-i\chi} + \alpha_2 e^{i\chi})^{-2}$  the sum of the three contributions

$$\frac{P^2 k^2}{m^2 e^4} + \frac{P^2 k}{2m^2 e^4} (P - k_2) + \frac{P^2 k}{2m^2 e^4} (P - k_1) = \frac{P^3 k}{m^2 e^4}.$$

This is the value of  $k/m\dot{w}$ . Hence

$$\dot{w} = me^4/P^3,$$

which happens to be the same function of  $P$  as on the classical theory. Now since  $H = -me^4/2P^2$ , we have

$$\dot{w} = \partial H / \partial P,$$

which proves that  $P$  is canonically conjugate to  $w$  and is therefore an action variable. The transition frequencies are now given by

$$\frac{H(P + nh) - H(P)}{h} = \frac{me^4}{2h} \left\{ \frac{1}{P^2} - \frac{1}{(P + nh)^2} \right\}. \quad (32)$$

The expansion of  $r$  is given by the expansion of the right-hand side of (31) in which the appropriate power of  $e^{i\theta}$  has been inserted behind each term. The coefficient of every term in it vanishes when one puts  $P = 0$ , which makes each of the amplitudes  $x(nm)$  in the c-number representation of the Cartesian co-ordinates vanish when  $n$  or  $m$  is zero. This suggests, according to the principles of § 4, that the state  $J = h$  is the normal state. (To prove this completely it would be necessary to show that  $x(nm) = 0$  when  $n$  is a negative integer and  $m$  a positive integer.) If this is so, one would have to put  $P$  equal to an integral multiple of  $h$  in (32), and one would then obtain the observed frequencies of the hydrogen spectrum.

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*An Investigation of Wireless Waves arriving from the Upper Atmosphere.*

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PART I.—THE DIRECTIONS OF THE FORCES IN WIRELESS WAVES AT THE EARTH'S SURFACE.

1. *Previous Paper and Continuation of the Work.*

In a previous paper (1) the authors drew attention to the desirability of obtaining some conclusive experimental evidence as to the actual path of travel of wireless waves between the transmitter and receiver. According to modern theory the upper portion of the earth's atmosphere acts in the nature of a deflecting medium, from which some or all of the energy reaching it from the transmitter is returned to the earth's surface, these downcoming waves having a variable plane of polarisation. It was thought to be possible to demonstrate the presence or absence of such downcoming waves by making measurements at the earth's surface of the directions of the forces in the resultant waves received. The method adopted for the determination of the direction of the electric force in waves from near-by transmitters gave a means of measuring the effective conductivity of the earth's surface for wireless frequencies. This conductivity was found to be of such a high value that on theoretical grounds it was shown that the possibility of distinguishing between downcoming waves and horizontally propagated waves by directional measurements of the resultant forces would be very difficult on the medium and longer wave-lengths employed in commercial wireless communication. This deduction was confirmed by measurements carried out during 1924 at the Slough station of the Radio Research Board. Operating on transmissions whose wave-lengths ranged from 2,600 to 9,000 metres and under conditions where it was known that the usual phenomena (including night effects) of long-distance wireless transmission were present, the results showed that the directions of the resultant electric and magnetic forces in the received waves provided no definite evidence for or against the existence of downcoming waves.

The apparatus originally set up at Slough has been in constant use from October, 1924, until December, 1925, for similar measurements. The transmissions from Leafeld on 12,400 metres and Nantes on 9,000 metres have been

kept under constant observation and occasional experiments have been carried out on other transmitting stations using wave-lengths about 5,000 metres. The results obtained have fully confirmed the deductions previously made.

### *2. Reconstruction of the Apparatus for Shorter Waves.*

Since the theory indicated that changes in direction of the resultant forces would be more easily detectable on shorter wave-lengths, it was decided to repeat the measurements under these conditions, and owing to the presence of several very suitable and continuous transmissions from broadcasting stations the wave-length band of 300 to 500 metres was selected. Owing to the fact that the power of these transmitting stations is very much less than those operating on the longer wave-lengths, an increase in the sensitivity of the receivers was necessitated. This together with the need for overcoming various instrumental errors of increased importance at shorter wave-lengths led to the construction of a new rotating coil receiver and to some modifications of the Hertzian rod receiver. The improvements effected are, however, only in matters of detail, and the principle of operation of both sets of apparatus remains unaltered.

### *3. Typical Results obtained with Rotating Rod and Coil.*

(a) *Electric Force.*—In the use of the Hertzian rod receiver the same procedure was adopted as formerly, viz. : to determine first the angle (A) by which the electric force departs from the vertical in a vertical plane perpendicular to the direction of travel, and second, the angle (B) by which the electric force departs from the vertical in the vertical plane of propagation of the wave.\* When taking observations in this manner in the day time it is found in the first position that the signal minimum is quite sharp and that the angle A can be determined to within a fraction of a degree ; and also that consecutive observations taken over a period of one or two hours give constant values of A, a maximum variation of less than  $2^{\circ}$  having been observed during several months' observations on three stations operating on wave-lengths of about 400 metres. In the second case, while the angle B can be measured to an accuracy of the order of  $1^{\circ}$ , the signal minimum is found to be not silent, but blurred to such an extent that it is necessary to swing the rod through about  $4^{\circ}$  to  $8^{\circ}$  in making a determination. Within the limits of accuracy of the

\* The angles A, B, C, D were termed  $\alpha$ ,  $\beta$ ,  $\lambda$ ,  $\delta$  respectively in the previous paper (ref. 1). This change in notation was necessitated by the symbols required in the later mathematical portion of the present paper.

apparatus the angle  $B$  is also found to be constant in the day time. The following table (I) gives the values of  $A_0$  and  $B_0$ , which are the mean day-time values of these angles as measured on three transmitting stations over a period of several months.

Table I.—Values of Normal Daylight Tilts of Electric Force.

1	2	3	4	5
Transmitting station.	Wave-length (metres.)	$A_0$ (degrees).	$B_0$ (degrees).	Value of ground conductivity ( $\sigma$ ) calculated from $B_0$ . (E.S.U.)
Cardiff .....	353	+ 0.1	+ 3.0	$0.79 \times 10^8$
London .....	365	+ 0.2	+ 2.7	$0.95 \times 10^8$
Bournemouth .....	386	+ 0.9	+ 2.8	$0.81 \times 10^8$
Birmingham .....	479	- 0.1	+ 2.3	$0.97 \times 10^8$

In the simplest case, for a wave travelling horizontally along the ground the value of  $A_0$  should be zero, and  $B_0$  should have a positive value equal to the forward tilt of the wave as determined by the conductivity of the ground and the frequency of the wave.

From the values of  $B_0$  the conductivity of the ground at wireless frequencies can be calculated, and the results are given in column 5 of the above table. The mean conductivity so obtained for wave-lengths between 350 and 480 metres is  $0.9 \times 10^8$  in E.S.U. While this is considered to be a more accurate determination than has hitherto been made at Slough, it is to be noted that the value of  $10^8$  was arrived at in the previous experiments as an average value for the South of England (see ref. 1).

The accuracy of the experiments is limited by the effects of surrounding objects, such as trees, on the directions of the forces in the arriving waves, and the fact that in the above table  $A_0$  can depart from 0 by  $0.9^\circ$  is considered to confirm the experience mentioned in the previous paper (ref. 1, p. 594) that the inclination of the electric force to the vertical, as measured with the portable apparatus, varied in different parts of the field at Slough. In the present case this error is of no serious consequence, since it has been found to be constant and quite negligible compared with the variable changes in the direction of the force.

When observations of the directions of the electric force are carried out in the neighbourhood of sunset, it is found that these directions are subject to

changes of a very erratic and sometimes quite large magnitude. In the case of the transmissions from Bournemouth these variations have been observed to begin at as long as two hours before sunset in the summer months. The nature of the variations is probably best represented by means of the graphs in fig. 1, which show the results of a set of observations taken over a period of 2 hrs. 40 mins., the individual observations having been made at half-minute intervals during this time. It is seen that both the angles A and B vary in a rapid and very erratic manner, the period of the approximately cyclical variations being from one to four minutes. During the observations it was noticed that the nature of the signal minimum was continually changing in the case of the angle A as well as B. At one instant the minimum will be quite sharp and well defined, while at a later instant it will become quite blurred, indicating a large rotating component in the particular force being measured. It appears that there is no obvious relation between the sharpness of the minimum and the departure of the angle from its normal day value. At times these variations were taking place so rapidly that it was not possible to follow them accurately owing to the large inertia of the rotating Hertzian rod.

It will be noticed that in the case of both A and B the direction of the tilts of the resultant forces are constantly changing sign, and that they are often of reverse sign to the normal direction. The fact that the values of A and B are at times greater than the theoretical value of  $B_0$  is considered to be strong evidence indicating that during the time of these variations some of the waves received are arriving in a downward direction. When the angle A departs from its normal direction by very large amounts, it would appear that the downcoming wave is largely horizontally polarised, i.e. with the electric force in a horizontal plane, and when B has a large value, the downcoming waves are largely polarised with the electric force in the vertical plane of propagation. Although the observed effects are subject to complications due to variations of phase and amplitude of the arriving waves, the results appear to demonstrate the presence of downcoming waves at night, these waves being polarised in a plane which is almost continually changing or rotating.

(b) *Magnetic Force*.—The frame coil receiver can be used in two ways. First with the plane of the coil locked in a vertical position it can be used as an ordinary direction-finder for the determination of the apparent bearing of a transmitting station; the departure of the bearing so obtained from the true great-circle bearing of the transmitter is designated by the angle C.\*

\* See note on p. 581.

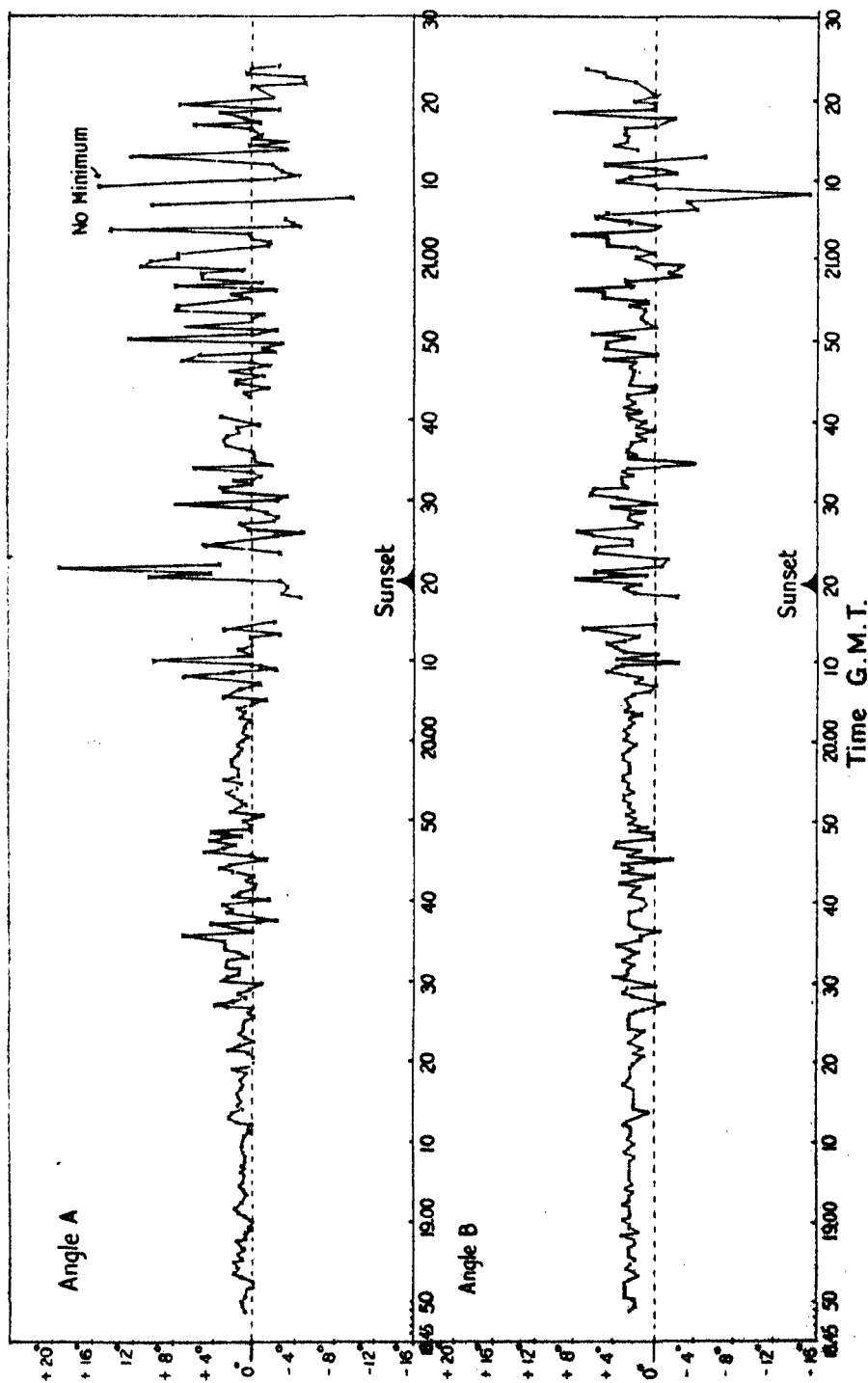
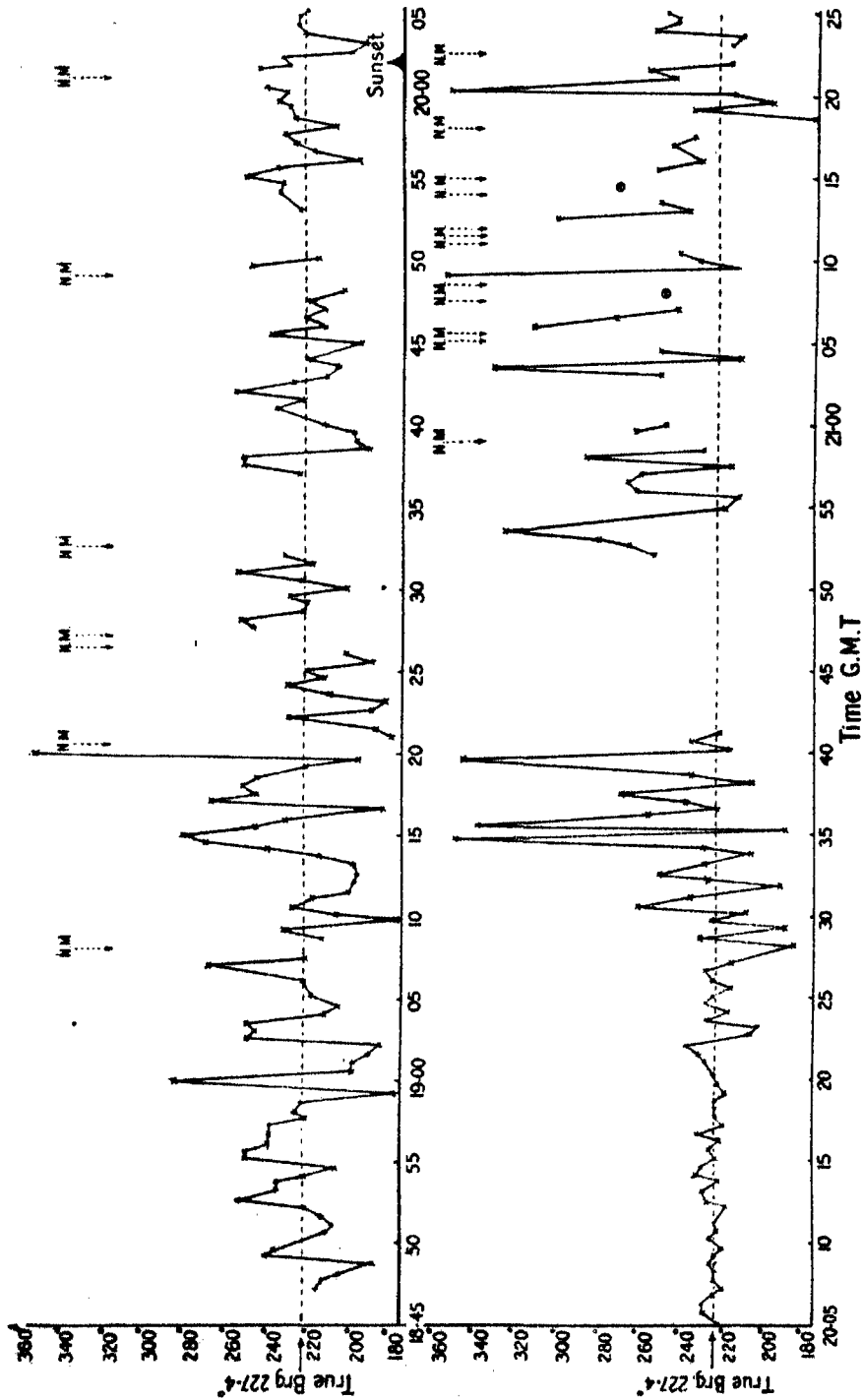


FIG. 1.—Observations of Angles A and B on Bournemouth, 18.6.25.  $\lambda = 386$  metres. Sunset, 20.20, G.M.T.





In the stable conditions prevailing during most of the daylight hours the observed bearing remains constant with an extreme variation of the order of  $\pm 1^\circ$ . The error in the mean bearing so obtained ( $C_0$ ) is the permanent error of the direction-finder under its conditions of use, and is attributable to the local conditions of the site. The values of  $C_0$  for three transmitting stations within the wave-length band employed are given below in Table II.

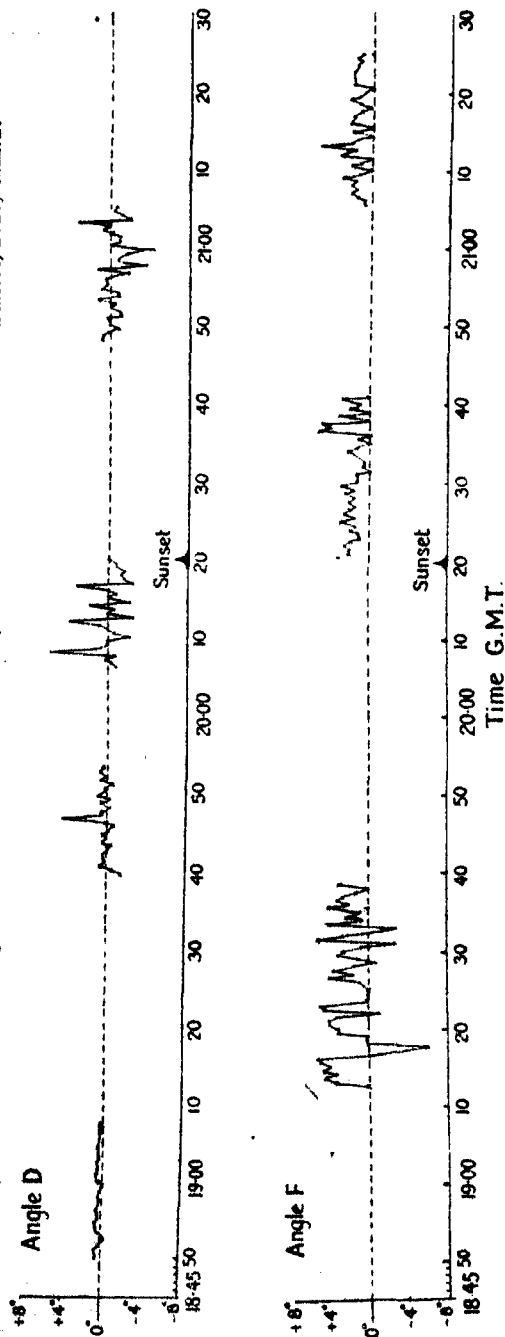
Table II.—Showing Error in Mean Day Bearings on Direction-Finder.

1	2	3	4
Transmitting station. {	Wave-length (metres).	True bearing (degrees).	Error in day bearing $C_0$ (degrees).
London .....	365	84.0	+ 1.2
Bournemouth .....	386	227.4	+ 4.0
Birmingham .....	479	319.1	+ 2.0

The second manner in which this frame coil receiver may be used is that of rotation about a horizontal axis set either parallel or perpendicular to the direction of propagation of the waves. Under the stable daylight conditions mentioned above it is found that this rotation produces a zero of signal intensity when the plane of the frame coil is horizontal. This indicates that the magnetic force of the arriving waves is in the horizontal plane, and repeated observations made under daylight conditions have shown that the maximum departure from the horizontal is less than  $1^\circ$ .

When, however, the observations are carried out in the proximity of sunset and during the hours of darkness, the direction of the magnetic force is found to vary in a most erratic manner. Considering first the variations in bearing, or the angle C, these are illustrated in fig. 2, which shows a typical series of readings taken at half-minute intervals for 2 hrs. 40 mins. during a sunset period. The time at which the variations begin approximately coincides with the beginning of the variations of angles A and B. The observations illustrated were taken at Slough on the Bournemouth transmitting station, and it is considered from previous experience that some coincidence of conditions is responsible for the excessive effects observed. It will be noticed that the apparent bearing varied at times over  $180^\circ$ , and on a few occasions it was noticed that the rotation was continued over a range of  $360^\circ$ . Further observations on other stations and wave-lengths will provide further

FIG. 3.—Observations of Angles D and F on Bournemouth, 18.6.25.  $\lambda = 386$  metres. Sunset, 2020, G.M.T.



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information for discussion of this point. As has been consistently observed in direction-finding work on wave-lengths in the neighbourhood of 450 metres, these variations are accompanied by a broadening of the signal minimum, which indicated that the horizontal component of the magnetic force has become of elliptical or circularly polarised form.

Accompanying the above variations, it is found that measurable tilts of the magnetic force to the horizontal are obtained on these shorter wave-lengths. With the horizontal axis of rotation in the direction of propagation, the angle D, which is the inclination of the coil to the horizontal for the minimum signal position, varies about  $4^\circ$  on either side. When the horizontal axis is set at right angles to the direction of propagation, the corresponding angle of inclination, F, is usually in the positive direction (see notation later) but varies over the range  $+5^\circ$  to  $-6^\circ$ . These last results are illustrated by the typical curves given in fig. 3.

2 R

In all cases it will be seen that the directions under observation are varying very rapidly, and it is at times difficult to make an accurate measurement. For example, the angle C, error in apparent bearing, has been observed to vary at the rate of  $160^\circ$  in 30 seconds.

(c) *Preliminary Conclusions from these Results.*—From the above typical results, which have been confirmed on many occasions, it may be stated that the extension of the experiments to shorter wave-lengths in accordance with the conclusions of the previous paper (*loc. cit.*) has been quite successful. It has been shown to be possible to obtain departures of the directions of both the electric and magnetic forces from their normal daylight values, which are measurable by means of the apparatus now employed. This is considered to establish directly the fact that at these times a portion of the energy received from the transmitting station has arrived in a downward direction and thus from the upper atmosphere. From the fact that the variations in the directions of both forces are obtained both in the plane of propagation and at right angles thereto, it may be deduced that the downcoming waves may be polarised either vertically or horizontally. Further, from the values of the angles actually measured, and also from the fact that on the direction-finding coil there is frequently no detectable minimum of signal strength, it may be concluded that the intensity of the wave is of the same order as that of the direct, horizontally propagated, wave.

#### 4. *Development of Apparatus for Additional Measurements on Received Waves.*

The experiments described in the previous section of the paper thus provide a satisfactory *qualitative* answer to the main question underlying the investigation, that is to say, they give conclusive proof (1) of the existence of downcoming waves in certain cases of the same order of intensity as that of the direct wave and arriving at a steep angle of inclination; (2) of the existence in these waves of an important horizontally polarised component. They do not by themselves, however, provide sufficient data for the calculation of the angle of incidence of the downcoming waves owing to the presence of the direct daytime wave, neither do they provide any means of calculating the relative intensity of the downcoming waves.

It appears, however, as shown in the theoretical discussion in section 5, that if, in addition, a measurement of the intensity of the resultant vertical electric force under normal and abnormal conditions could be made, enough information for a calculation of the angle of incidence would be provided.

As a preliminary to a further advance it was, therefore, decided to develop a suitable method of measuring this component (Z). This was successfully achieved by employing a receiver connected to a tuned vertical aerial and horizontal earth screen working in conjunction with a three-stage high-frequency amplifier, and a detector valve with a sensitive moving coil mirror galvanometer in its anode circuit, the steady anode current through the galvanometer being balanced out by a potentiometer arrangement. The amplifying circuit and galvanometer was calibrated by means of a local valve oscillator adjusted to give a constant output current. As the absolute value of the vertical electric force was not required, there was no need to know the absolute value of the current. It was found with this apparatus that the relative value of Z could be determined to within 10 per cent., while moment to moment changes could be faithfully recorded provided the rate of change was not excessive.

The Hertzian rod and signal-strength apparatus together provide sufficient information for the calculation of the angle of incidence of vertically polarised downcoming waves. In order to measure this quantity in the case of horizontally polarised waves the tilting-coil apparatus, as described in the earlier paper, was adapted for working on the shorter wave-lengths now being investigated.

When using this apparatus for the determination of the angle F, the coil is in such a position that the normal direct wave is eliminated. Thus the resulting tilt of the magnetic force to the horizontal is entirely the result of the downcoming waves; and its angle is in fact exactly equal to the *optical angle of refraction* of that wave at the earth's surface (see section 5). Hence from the ordinary optical laws of reflection and refraction the angle of incidence can at once be calculated provided the electrical constants of the earth in the neighbourhood of the receiver be known.

Thus two methods of measuring the angle of incidence of the downcoming waves were available and working satisfactorily. They both, however, suffer from the same two drawbacks; first, that they involve the measurement of residual effects which for longer waves are negligibly small and which are only just measurable with the wave-lengths now employed; and, secondly, that they depend on a knowledge of the electrical constants of the ground in the neighbourhood of the receiver, which are by no means accurately known. For these reasons neither of these methods is very accurate.

The need of an alternative method was therefore strongly felt, particularly of a method which should be independent of the value of the ground constants and should not involve the measurement of quantities rendered residual on account of the reflecting power of the earth's surface. It had been realised

for some time that such a method existed, but owing to experimental difficulties, among other reasons, it had been temporarily laid aside. It was now thought desirable to develop it, and after a few months' work the method was successfully put into use. The resultant electro-magnetic fields produced at the surface of a perfect conductor by a wave travelling along that surface and by a wave inclined to it, are completely indistinguishable from one another in respect to their direction, but differ in this important respect, that whereas in the former case the electric and magnetic force are equal, in the latter case the magnetic force is greater than the electric force, the ratio of the two intensities being dependent on the angle of incidence of the wave.\* As shown in section 5, if  $Z$  be the resultant vertical electric force of the wave whose angle of incidence is  $\theta$  and  $\beta$ , its resultant horizontal magnetic force at right angles to its plane of propagation, the relation

$$\frac{\beta}{Z} = \frac{1}{\sin \theta}$$

holds good *whatever the nature of the surface on which the wave is incident and for all wave-lengths.*

The practical method of measuring this ratio and thus obtaining  $\theta$  is shown in fig. 4. It consists in comparing the instantaneous value of the signal strength induced respectively in a closed loop and a vertical aerial. The loop and aerial are alternately switched on to the respective field coils of a radio-goniometer by means of a switch operated by a single movement. The search coil is meanwhile rotated until a balance is obtained. The tangent of the angle which the search coil now makes with its original position is then proportional to the ratio of the current in the aerial to that in the loop, and this ratio is proportional to  $\beta/Z$ , provided that the loop is aligned in the direction in which the wave is travelling. The datum value of this ratio is obtained by calibrating the system on a wave which can be safely assumed to be travelling horizontally and for which therefore  $Z = \beta$ . It must be realised that though this method is superior to the Hertzian rod and tilting coil methods in that it is unaffected by the nature of the earth surface and of the lengths of the waves under investigation, yet in common with the Hertzian rod apparatus it cannot be

\* Since the above was written, a paper has been published by Appleton and Barnett ('Roy. Soc. Proc.,' A, vol. 109, p. 621 (1925)), describing experiments in which this principle was used to detect the existence of waves arriving at the receiver in a direction inclined to the horizontal. The experiments showed that the fading of wireless signals was greater on a loop than on an aerial, and from the ratio of the respective variations the angle of incidence of the downcoming waves was calculated.

used to calculate  $\theta$  without a knowledge of the ratio of the intensity of the direct wave to that of the downcoming wave, and it is therefore necessary, as in the former case, to make simultaneous observations of the relative intensity of the vertical electric force under normal and abnormal conditions.

In employing the loop-aerial apparatus for the determination of the angle of the downcoming waves, the loop as already mentioned is aligned in the direction of the transmitter. By aligning it at right angles to this direction another ratio can be determined, *i.e.* the ratio of the vertical electric force ( $Z$ )

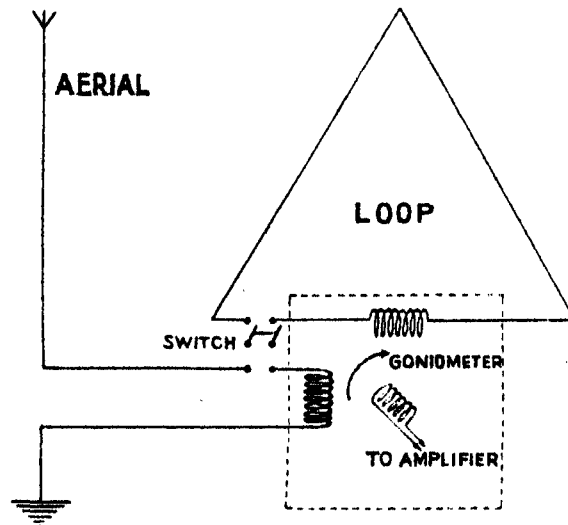


Fig. 4.—Method of Measuring the Ratio  $\frac{\text{Magnetic Field}}{\text{Electric Field}}$

to the magnetic component ( $\alpha$ ) parallel to the wave direction. This latter component is, of course, zero for horizontally travelling waves, and, in fact, for all vertically polarised waves not laterally deviated. But it becomes finite when there is present a downcoming wave with a horizontally polarised component and in this case the ratio  $\alpha/Z$ , though not giving the angle of incidence directly, can give valuable information as to the intensity of the horizontally polarised portion of the waves (see section 5). In practice, therefore, a second loop was erected at right angles to the first, and by means of a suitable switch the two ratios  $\beta/Z$  and  $\alpha/Z$  were measured alternatively throughout the experiments.

PART II.—AN INVESTIGATION OF THE INTENSITY AND ANGLE OF INCIDENCE OF DOWNCOMING WAVES.

5. *Theoretical Discussion of the Effects of Downcoming Waves.*

(a) *Notation.*—In order to show the relation between the quantities determinable by the various experimental apparatus above described and the quantities we wish to calculate (*i.e.* angle of incidence and intensity of downcoming waves), it now becomes desirable to give a brief mathematical discussion of the whole problem. In this discussion the following notation will be used:—

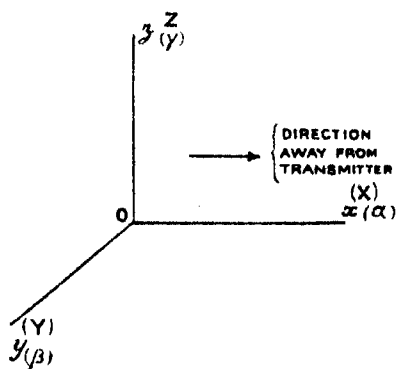


FIG. 5.

It is supposed that the electromagnetic field is under investigation at the origin (O, fig. 5) of a system of coordinates chosen so that:

Ox is along the great-circle path from transmitter to receiver.

Oy is the horizontal direction perpendicular to Ox.

Oz is vertical.

Let X, Y, Z, be the components of the total electric force at O,

$\alpha$ ,  $\beta$ ,  $\gamma$ , be the components of the total magnetic force at O,

and let

X', Y', Z', etc., refer to the field components in the ground.

K = dielectric constant of ground,

$\sigma$  = conductivity in electrostatic units,

$n$  = frequency, and

$$K' = K - \frac{2i\sigma}{n}.$$

This quantity  $K'$  is employed in the analysis whenever the field in the earth itself is under consideration. It then plays exactly the same part with regard to the conducting medium as the dielectric constant K would play in the case of a non-conductive medium.

Thus  $\sqrt{K'}$  is the optical refractive index of the earth's surface.

By means of the above notation we can now define more precisely the quantities measured experimentally by the various apparatus employed,\* viz.:—

\* This assumes the two vectors are in phase and will, therefore, only hold good when the reading is a sharp one.

*Hertzian rod apparatus*, determines  $X/Z$  ( $\tan^{-1} B$ ), and  $Y/Z$  ( $\tan^{-1} A$ ).

*Tilting coil apparatus* determines  $\alpha/\beta$  ( $\tan^{-1} C$ ),  $\gamma/\beta$  ( $\tan^{-1} D$ ),  $\gamma/\alpha$  ( $\tan^{-1} F$ ).

*Signal-strength apparatus* determines  $Z$  (relative values).

*Loop and aerial apparatus* determines  $\alpha/Z$  and  $\beta/Z$ .

In order to find the relation between these quantities and the angle of incidence ( $\theta$ ) of the downcoming wave, several special cases must now be considered.

(b) *Case of a Single Downcoming Wave, vertically polarised.*—Let a wave of this description travelling in the plane  $zOx$  arrive at angle of incidence ( $\theta$ ) (fig. 6). Let  $E_1$  be the amplitude of electric field of the incident wave, and let  $\phi$  be angle of refraction.

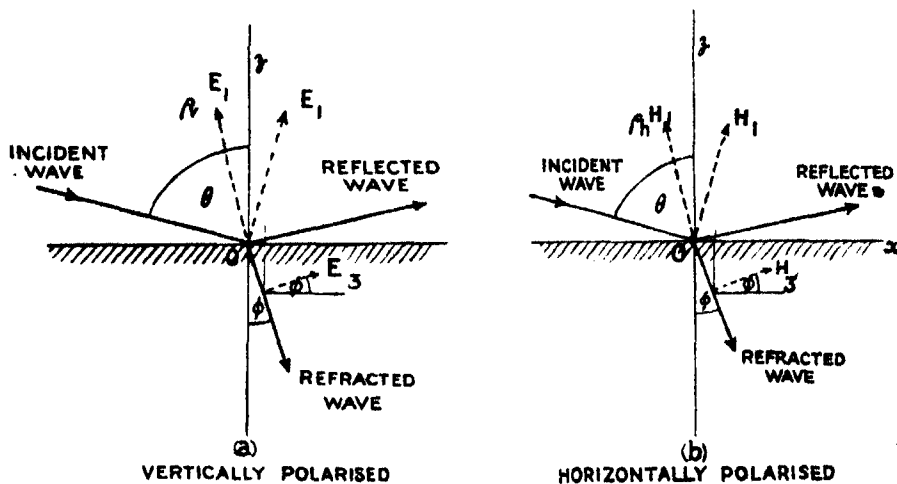


FIG. 6.—Single Downcoming Waves.

Since the wave is vertically polarised, we have

$$Y = \alpha = \gamma = 0.$$

At the earth's surface the boundary conditions demand that the tangential components of force in the two media shall be equal and that the normal components of induction shall also be equal, i.e. that (assuming for air  $K = \mu = 1$ ; for earth  $\mu' = 1$ ):

$$\left. \begin{aligned} X &= X' \\ \beta &= \beta' \\ Z &= K' Z' \end{aligned} \right\} \quad (1)$$

Therefore

$$\frac{X}{Z} = \frac{X'}{K' Z'} = \frac{1}{K'} \cot \phi. \quad (2)$$



Now from optical laws and also from standard electro-magnetic theory we have

$\frac{\sin \theta}{\sin \phi} = \sqrt{K'}$  so that eliminating  $\theta$  we get

$$X/Z = 1/K' \frac{\sqrt{1 - \frac{\sin^2 \theta}{K'}}}{\frac{\sin \theta}{\sqrt{K'}}}. \quad (3)$$

Now under the particular conditions of these experiments  $K' \gg 1$ , so that the right-hand numerator is approximately unity.

Hence :

$$\frac{X}{Z} = \frac{1}{\sqrt{K'} \sin \theta} \quad (4)$$

Now in the special circumstances of a normal "horizontally" travelling wave (i.e. the direct wave) there will be no reflected wave.

So that we must have

$$\frac{X_0}{Z_0} = \cot \theta. \quad (5)$$

Eliminating  $\theta$  in (3) by means of (5), we find that the expression (3) reduces to the exact relation,

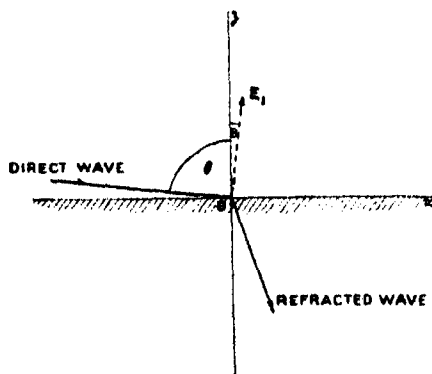


FIG. 7.—Special Case ;  $\rho_n = 0$  (Direct Wave).

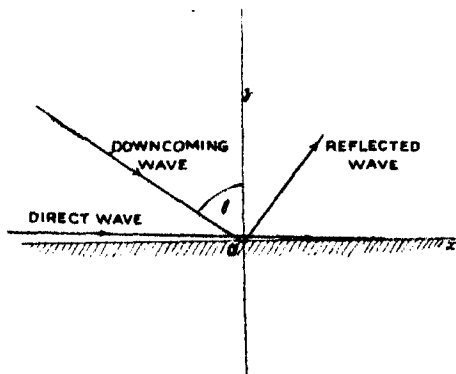


FIG. 8.—Case of Two Arriving Waves.

$$\frac{X_0}{Z_0} = \frac{1}{\sqrt{K'}}, \quad (6)$$

which is identical with Zenneck's expression for the forward tilt of a wave, and is, in fact, the reciprocal of the refractive index of the medium (see fig. 7).

We also have from fig. 8,

$$\left. \begin{aligned} X &= E_1 (1 - \rho_v) \cos \theta \\ Z &= E_1 (1 + \rho_v) \sin \theta \\ \beta &= H_1 (1 + \rho_v) \end{aligned} \right\}, \quad (7)$$

where  $\rho_v$  = the reflection ratio of the earth at the angle of incidence  $\theta$ , and frequency of the waves employed.

From (7) we get at once,

$$\frac{\beta}{Z} = \frac{1}{\sin \theta}. \quad (8)$$

( $\beta/Z$ , it will be remembered, is the ratio measured by the loop-aerial apparatus described in the last section (4).)

(c) *Case of a Single Downcoming Wave, horizontally polarised.*—In this case  $Z = X = \beta = 0$  by hypothesis.

The boundary conditions, as before, require continuity of tangential force and normal induction on crossing the boundary surface, i.e.

$$\left. \begin{aligned} Y &= Y' \\ \alpha &= \alpha' \\ \gamma &= \gamma' \end{aligned} \right\}, \quad (9)$$

so that we see at once (since the permeability of both media is unity)

$$\gamma/\alpha = \gamma'/\alpha' = \tan \phi, \quad (10)$$

but  $\gamma/\alpha = \tan F$  ( $F$  being the angle measured by the tilting coil as described in section 4).

Hence

$$F = \phi. \quad (11)$$

That is, we are, by this method, making a direct measurement of the angle of refraction of the waves.

The relation between  $F$  and  $\theta$  is given by

$$\begin{aligned} \tan F &= \gamma/\alpha = \tan \phi \\ &= \frac{\sin \theta}{\sqrt{K'}} \times \frac{1}{\sqrt{1 - \frac{\sin^2 \theta}{K'}}}, \end{aligned}$$

therefore

$$\tan F = \frac{\sin \theta}{\sqrt{K'}} \quad (12)$$

under the condition, satisfied throughout these experiments, that

$$\sqrt{K'} \gg 1.$$

(d) *General Case of Single Wave.*—If we combine the two preceding cases we get the general case of a single arriving wave polarised in any plane, or circularly or elliptically polarised. For such a wave it will be seen at once that equations (1) to (12) are still valid.

(e) *Case of Two Arriving Waves—Direct and Downcoming.*—In practice, when downcoming waves are being received, there will sometimes be at least two waves arriving simultaneously—the first the direct horizontally propagated wave and the second the downcoming wave (see fig. 8). Of course, there may be two or more downcoming waves, but we will at first consider only one.

Let  $\theta$  be angle of incidence of downcoming wave. (That of direct wave =  $90^\circ$  approx.)

Let  $E_0, X_0, Y_0, Z_0$ , etc., refer to electro-magnetic field of direct wave.

$E_1, X_1, Y_1, Z_1$ , etc., refer to resultant field produced by the downcoming wave, together with reflected wave.

Then from equation (4), (6), (8), (12),

$$\left. \begin{aligned} \frac{X_0}{Z_0} &= \frac{1}{\sqrt{K'}}; & \frac{X_1}{Z_1} &= \frac{1}{\sqrt{K'} \sin \theta} \\ \frac{Z_0}{\beta_0} &= 1 \text{ (approx.)}; & \frac{Z_1}{\beta_1} &= \sin \theta \\ \frac{Y_0}{\alpha_0} &= 0/0; & \frac{Y_1}{\alpha_1} &= \frac{\sin \theta}{\sqrt{K'}} \end{aligned} \right\}. \quad (13)$$

We also have the vectorial relation :

$$\left. \begin{aligned} X &= X_0 + X_1 \\ Z &= Z_0 + Z_1 \\ \alpha &= \alpha_0 + \alpha_1 \\ \beta &= \beta_0 + \beta_1 \end{aligned} \right\}. \quad (14)$$

So that from (13) and (14) we finally obtain the following three independent expressions for  $\sin \theta$  :—

$$\text{(Hertzian rod quantities)} \sin \theta = \frac{1}{\sqrt{K'}} \left( \frac{Z - Z_0}{X - X_0} \right), \quad (15)$$

$$\text{(Tilting coil quantities)} \sin \theta = \sqrt{K'} \left( \frac{\gamma - \gamma_0}{\alpha - \alpha_0} \right) = \gamma / \alpha \sqrt{K'}, \quad (16)$$

$$\text{(Loop and aerial quantities)} \sin \theta = \left( \frac{Z - Z_0}{\beta - \beta_0} \right), \quad (17)$$

where the magnitudes of all the vectors on the right-hand side of these equations are determinable by experiment, in some cases directly and in others indirectly.

Of these three methods it will be noticed the third is independent of  $K'$ ; the second is independent of the nature of the direct wave; whilst the first

has neither of these advantages. To obtain a numerical value for  $\theta$  from (15) and (17), it is necessary to know the phase relation  $X$  between the downcoming and direct waves. As it is quite impossible at present to measure  $X$  directly, it is necessary to select from the experimental results only those observations for which a definite assumption of the value of  $X$  can be made. The discussion of how far this can be done and how it affects the accuracy of determination of  $\theta$  is conveniently left until the section dealing with the actual results obtained (p. 601).

It is further to be noted that of the above three methods of measuring the angle of incidence, the second, making use of equation (16), applies only to the horizontally polarised portion of the downcoming waves, while the other two apply to the vertically polarised waves.

(f) *Relative Intensities of Direct and Downcoming Waves.*—It is also possible from these equations to find simple expressions for the relative intensities of the downcoming wave in terms of the intensity of the direct wave. Thus, for the vertically polarised component :—

$$E_1 = \frac{Z_1}{(1 + \rho_r) \sin \theta}$$

from (7) and  $E_0 = Z_0$  approximately, so that

$$\frac{E_1}{E_0} = \left| \frac{Z - Z_0}{Z_0 (1 + \rho_r) \sin \theta} \right|, \quad (18)$$

and for the horizontally polarised component by reasoning similar to that from which (7) was obtained

$$\begin{aligned} \alpha_1 &= H_1 (1 + \rho_h) \cos \theta \\ &= E_1 (1 + \rho_h) \cos \theta, \end{aligned}$$

where  $\rho_h$  is the reflection ratio of the earth for horizontally polarised waves arriving at angle of incidence  $\theta$ .

Also

$$E_0 = Z_0 = \beta_0.$$

Thus

$$\frac{E_1}{E_0} = \frac{\alpha_1}{Z_0} (1 + \rho_h) \cos \theta \quad (19)$$

$$\alpha_1 = \alpha - \alpha_0 = \alpha$$

$$\frac{E_1}{E_0} = \alpha/Z \times Z/Z_0 \times \frac{1}{(1 + \rho_h) \cos \theta} \quad (20)$$

All the quantities on the right-hand side of (19) and (20) can be either determined experimentally or calculated from known data. The reflection ratios  $\rho_v$  and  $\rho_h$  are determined from the simple Fresnel's optical reflection formulæ.

$$\rho_v = \frac{\tan(\theta - \phi)}{\tan(\theta + \phi)} \quad (21)$$

$$\rho_h = \frac{\sin(\theta - \phi)}{\sin(\theta + \phi)} \quad (22)$$

where  $\phi$  is the angle of refraction given by

$$\frac{\sin \theta}{\sin \phi} = \sqrt{K'}.$$

(g) *Case of More than one Downcoming Wave.*—While in the above analysis we have assumed that there is only one downcoming wave, it is clearly necessary to envisage the possibility of more than one. In such a case the field components  $E_1$ ,  $X_1$ ,  $Y_1$ , etc., of the above equations must be taken as representing the sum of the individual components due to all the downcoming waves present. If all these waves arrive with the same angle of incidence there is obviously no difference between this case and the former case, and there is no need to distinguish between them, or in fact possibility of doing so. If, however, they are arriving at different angles of incidence  $\theta_1$ ,  $\theta_2$ ,  $\theta_3$ , etc., the angle  $\theta$  determined from equations (15), (16), (17), will represent only a mean or resultant angle of incidence. This mean will naturally be biased towards the wave of greatest intensity. It will also be affected by the relative phases of the component waves, and in certain critical cases (i.e. when the vector sum of the intensities approaches zero) it can conceivably give an entirely misleading or impossible value for  $\theta$ : a value, for instance, not even lying between  $\theta_1$ ,  $\theta_2$ ,  $\theta_3$ , etc. The discussion of the possibility of eliminating such misleading cases must again be left until the experimental results are under consideration (see Section 8).

(h) *Conclusions from the Above Analysis.*—From this analysis the conclusions were therefore drawn that the angle of incidence of the resultant downcoming wave could be obtained with the apparatus available in three independent ways, viz. :—

1. By the Hertzian rod apparatus provided the ground constants (refractive index) were known and that a definite value could be assumed for the phase difference between the direct and downcoming waves.
2. By the tilting coil apparatus provided the ground constants were known but *without any knowledge of the nature or phase of the direct wave.*
3. By the loop-aerial method provided the phase assumption can be made, but *independently of the value of the ground constants.*

Since no two of these three methods are dependent on the same proviso, they clearly form valuable checks on each other.

The analysis further shows that the relative intensity of the resultant down-coming wave can be calculated when once  $\theta$  has been determined.

Of the assumptions underlying the analysis only one was at all open to doubt. The nature of this assumption and the means by which it was checked are dealt with in the next section (6).

#### *6. Investigation of Lateral Deviation of Arriving Waves.*

One of the assumptions on which the foregoing analysis is based has had hitherto little or no experimental evidence to support it. This assumption is that all waves arriving at the receiver are propagated in the plane of  $z O x$  — the vertical great-circle plane between transmitter and receiver. If there were any serious lateral deviation from this plane, the simple relationship between the angle of incidence and the quantities measured (equations (15), (16) and (17)) would no longer hold, and further analysis shows that it would be extremely difficult if not impossible to determine  $\theta$  under such conditions.

An experimental verification of this assumption is therefore highly desirable. In the case of a wave entirely polarised in a vertical plane, an ordinary rotating coil direction-finder suffices to determine the angle of lateral deviation ( $\psi$ ), but this method breaks down if the wave has a component polarised in a horizontal plane.

Although devised chiefly with a view to reducing interference or the variable errors of direction-finders, several arrangements have been described which provide methods of measuring  $\psi$ , but though sound in theory they are surrounded by many experimental difficulties. It was to the overcoming of these difficulties that attention was directed in the present investigation, and after a considerable amount of research in this direction one of Adcock's suggested methods (3) was made to work with sufficient accuracy for the purpose in hand.

The arrangement comprised four vertical wire Hertzian receivers 40 feet high, erected at the four corners of a square of 20 feet side, and leads from their centres brought to the field coils of a goniometer, which with the rest of the receiving apparatus and operator were in a hut above the ground so as to be as near as possible to the electrical centre of the system. The two aerials at the extremity of each diagonal formed a pair connected to one of the field coils but in opposite senses, so that at any instant the current through the

field coil, due to one of the aeriels in the pair, would be in the opposite direction to that produced by the other member of the pair.

A simple consideration of this arrangement shows that the ratio of the currents in the field coil of the goniometer gives the tangent of the angle of lateral deviation, and this ratio as in the ordinary Bellini-Tosi D.F. System is given by the tangent of the scale angle of the search coil.

If there is more than one wave arriving, the method will give a mean angle of lateral deviation.

A series of experiments were made on those transmitting stations for which  $\theta$  was measured, and the result substantially confirmed the assumption made in the analysis that the lateral deviation was negligibly small.

It may be pointed out that if it can be satisfactorily demonstrated that the arriving waves are not subject to any lateral deviation at periods when errors are obtained on a direction-finder, this would constitute another independent proof of the arrival of downcoming waves and of the rotation of the plane of polarisation of such waves.

#### *7. Description of Experiments made on Transmissions from Bournemouth Station.*

We have seen from section 4 that four sets of apparatus have been devised for measuring separate quantities connected with the resultant electro-magnetic field of the arriving waves, and that these together provide three methods of measuring the angle of incidence of the downcoming wave ; also that the intensity of the downcoming wave can be determined at any instant when the angle of incidence is known.

After some preliminary experiments carried out during the early months of the year, it was decided to make all four sets of observations simultaneously. Each apparatus was accordingly set up in the large field at the Radio Research Station at Slough, at distances from each other of about 100 yards. A system of routine observations was started in May, 1925, concentrating on the B.B.C. station at Bournemouth, 77 miles distant, operating on a wave-length of 386 metres. On one day per week simultaneous observations were taken on all four sets of apparatus for a period of about an hour and a half some hours before sunset, and for a period of about three hours extending through sunset. The first of these periods enabled the daytime values of the quantities being determined to be established (these values, as has been seen, being essential to the determination of  $\theta$ ), and also gave a satisfactory idea of the limits of

accuracy of the apparatus. The second of these periods covered the transition period from the normal daytime conditions to the state of affairs brought about by the arrival of downcoming waves, and thus gave results which, coupled with those obtained in the first period, enabled the angle of incidence of the downcoming waves to be calculated. Simultaneous readings were taken on each instrument every half minute during the period of working, great care being taken to synchronise the watches of the four observers. But in addition to this an occasional rapid series of observations was made in which readings were taken once every five seconds, in order, in the first place, to obtain a rough idea of the maximum rate at which variations were taking place in the quantities being measured, and, in the second place, to obtain better synchronisation of the observations.

8. *Summary of Results obtained on Bournemouth ( $\lambda = 386$  metres) from May to July, 1925.*

After the observations had been made they were recorded in the form of curves. Each quantity was plotted on a separate sheet, but the time scale on each sheet was the same in order that the variations could be readily compared. During the period under discussion a large quantity of data was collected, and while it is, of course, not necessary to reproduce all the curves a selection has been made, and is reproduced in this paper in order to illustrate the general nature of the phenomena observed and to give an example of the data from which the angle of incidence of the downcoming waves was deduced.

(a) *Curves of Z.*—The daytime value was found to be steady to within 10 per cent., and as it is not certain whether the variations within this limit are due to actual signal-strength variations or to instrumental causes, this must be taken as the limit of accuracy of the apparatus. The observations in this case were made every fifteen seconds.

Fig. 9 shows results obtained at night, the observation being taken at intervals of 30 seconds. Variations begin to be appreciable at least one hour before sunset. The variations are small at first, but increase steadily until they reach a maximum amplitude of about 70 per cent. of the day value. The fading oscillations show a tendency to be asymmetrical about the mean, the positive peaks being greater than the negative.

Fig. 10 shows the results of a rapid test in which readings were taken every five seconds for a period of five minutes, the curve is plotted on the same sheet as similar curves taken simultaneously of the value of  $\beta/Z$ . The curve of  $Z$  shows that during this particular period the rate at which variations took place



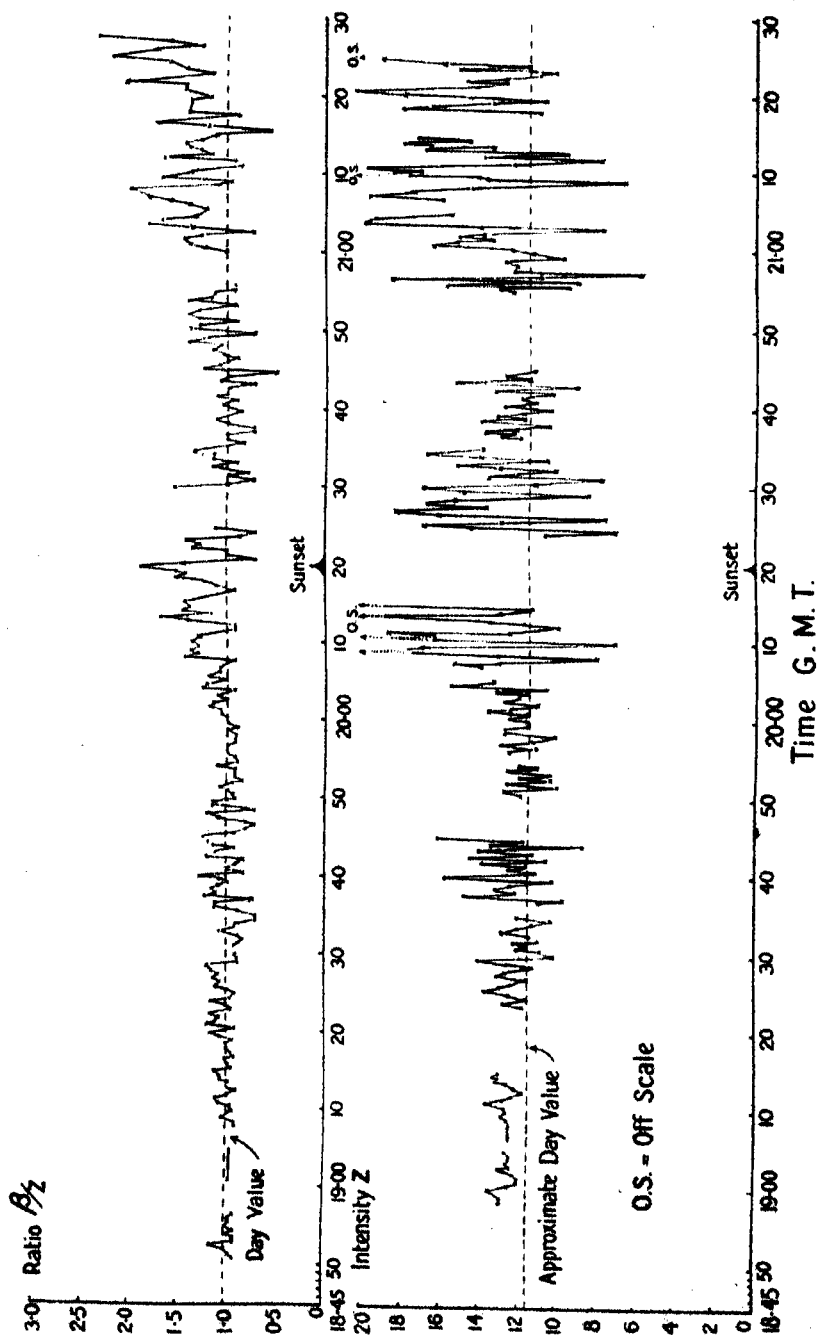


FIG. 9.—Observations of  $\beta/Z$  and Z on Bournemouth, 18.6.25.  $\lambda = 386$  metres. Sunset 2020, G.M.T.

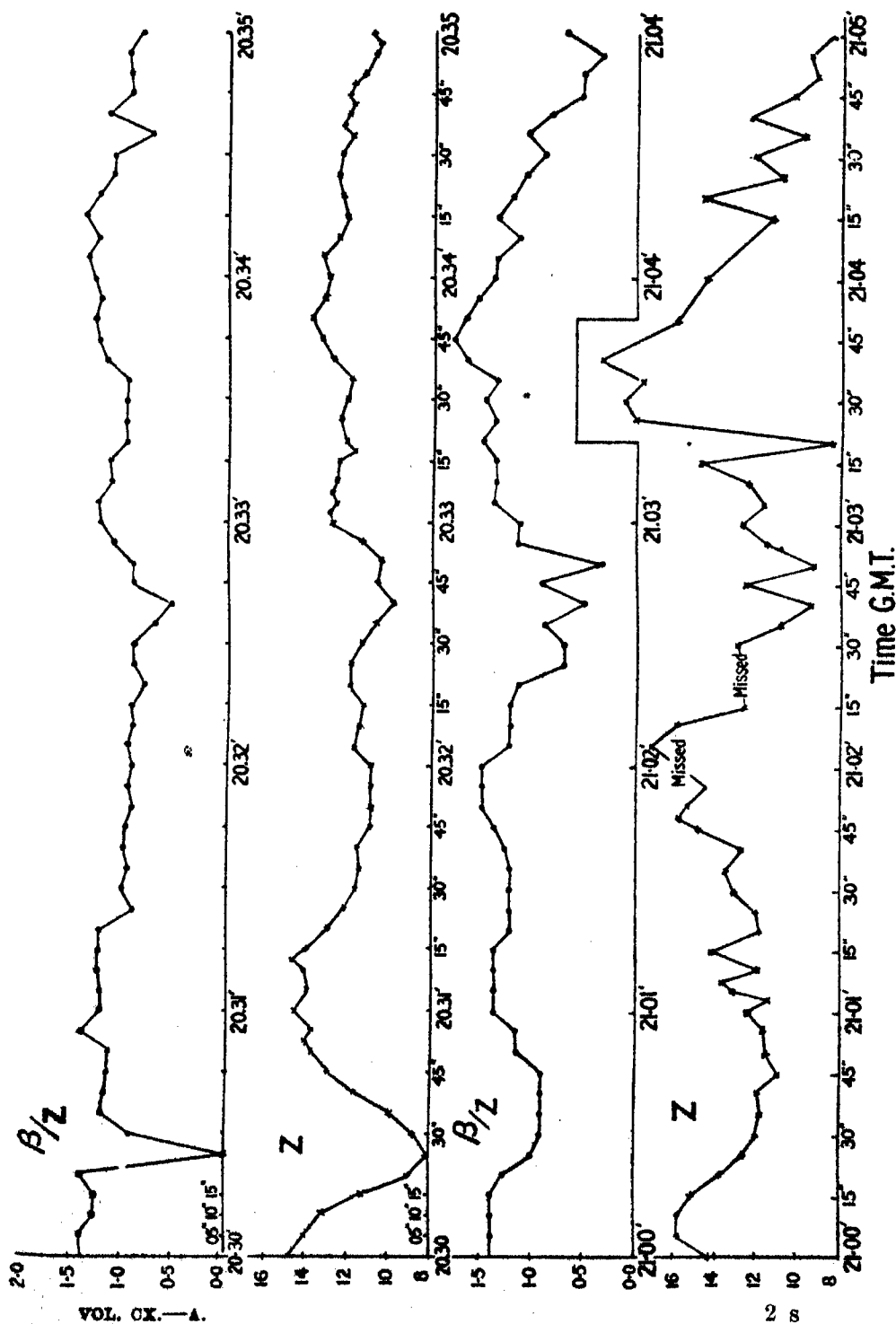


FIG. 10.—Simultaneous Observations of  $\beta/Z$  and Z on Bournemouth, 25.6.25.  $\lambda = 386$  metres. Sunset, 2021, G.M.T.  
Special Rapid Tests. Readings every 5 seconds

was on the average from 10 to 20 per cent. in 5 seconds, while on the other hand on one occasion it was as great as 100 per cent. in 5 seconds.

(b) *Curves of Angle B.*—In fig. 1 was shown curves taken of the value of the angle B simultaneously with those of Z in fig. 9. The day value of the angle B remains constant to less than a degree, except for isolated little peaks. The night values (fig. 1) show signs of appreciable changes at about the same time before sunset as in the case of Z. The preliminary variations are followed by a distinct "lull" just before sunset, as in the case of Z, after which they start again and increase to their maximum. They are distinctly asymmetrical, tendency always being for the tilt to increase. Negative values of B are not very frequent, but they certainly occur from time to time. The tilt often exceeded  $5^\circ$ , on a few occasions rose to  $8^\circ$ , and once to  $15.5^\circ$ . On comparing these figures with simultaneously obtained Z curves, no definite correspondence can be traced.

No rapid tests could be taken of the value of B, for, owing to the inertia of the beam carrying the aerial, it was impossible to take readings once every five seconds. It is therefore difficult to gauge the rate at which the variations were taking place, but as far as could be judged they were too quick to be followed continuously.

(c) *Curves of Angle F* ( $\tan^{-1} \gamma/\alpha$ ).—Fig. 3 showed an example of the results obtained from a measurement of the angle F. This angle cannot be measured in the day-time, as the signal strength is zero for all inclinations of the coil. At night it is only possible to obtain a reading when the signal strength in the day minimum position of the coil is of the same order as the strength in the maximum position, i.e. when the minimum is very flat or the error in bearing very large. This figure illustrates well the general results obtained. The variations are almost all confined to the positive side of the zero, corresponding to a forward tilt of the magnetic field. The variations rarely exceed  $+4^\circ$ . There is a distinct tendency for the angle to settle down at a steady value of about  $+2^\circ$ , even though during this steady state Z, B, and  $\beta/Z$  may be varying greatly. Reference to the  $\alpha/Z$  curves show that this steady value is invariably accompanied by large values of  $\alpha/Z$  of same order as  $\beta/Z$ .

The variations of F are unique in that they tend to get small when the others, B, Z,  $\beta/Z$ , and  $\alpha/Z$ , etc., get larger.

It is interesting to point out here that in seeking for evidence of a down-coming wave, Eckersley (2) effectively measured the ratio  $\gamma/\alpha$  by comparing the E.M.F.'s induced in a horizontal and a vertical loop by the incoming waves at such times as the latter gave an error in the apparent bearing of the trans-

mitting station. Experimental results obtained at a receiving station near Cairo indicate that on a wave-length of 2,600 metres the magnetic field of the arriving waves was tilted at an angle which was not more than  $2^\circ$  from the horizontal at times when the usual night effects were present.

(d) *Curves of Ratio  $\beta/Z$ .*—Figs. 9 and 10 show typical curves obtained from a measurement of the ratio  $\beta/Z$ . The day variation was found to be within 10 per cent., and this may be taken as the limit of accuracy of the apparatus. Night variations (fig. 9) start at about an hour before sunset, as with the others, and in this case also steady down just before sunset. The night variations, when small, are roughly symmetrical about the mean daytime value. As, however, they get larger they become distinctly asymmetrical, the tendency always being for  $\beta/Z$  to be greater than unity (its normal value). Nevertheless, on rare occasions the value dips almost to zero. In fig. 10 is shown the result of a rapid test carried out simultaneously with the  $Z$  curve on the same diagram. The two curves show very satisfactory agreement, the two values quite clearly increasing and decreasing together. This indicates that the observations were quick enough to follow the variations of both  $Z$  and  $\beta/Z$  continuously.

#### 9. Calculation of Angle of Incidence of Downcoming Waves.

(a) *Hertzian Rod Method (Angle B).*—As has been shown in the theoretical analysis (section 5), the relation between  $\theta$  and the quantities measured by the Hertzian rod apparatus is given by

$$\sin \theta = \frac{1}{\sqrt{K'}} \left| \frac{Z - Z_0}{X - X_0} \right|. \quad (15)$$

This relationship, however, only holds good at the surface of the earth, whereas the centre of the Hertzian rod which measured  $B$  was 20 feet above the ground. This fact necessitates the introduction of an important correction factor  $C_A$  which allows for the phase displacement which must exist between the reflected and incident wave at a point above the ground.

The relation (15) thus becomes

$$\sin \theta = \frac{1}{\sqrt{K'}} \left| \frac{Z - Z_0}{X - X_0} \right| \cdot C_A. \quad (15a)$$

$C_A$  is a simple function of the height above the ground, the wave-length, and the angle of incidence. For the particular height in question (*i.e.* 20 feet) the value of  $C_A$  varies from about 1 to 2.5 as  $\left| \frac{Z - Z_0}{X - X_0} \right|$  decreases from 16.5 to 2.5.

If the angle  $B$  is sharply defined, it may be assumed that

$$\tan B = X/Z \text{ approx.,}$$

and also that the two waves are approximately in phase; so that the vector quantities in 15a can be treated as scalar quantities in order to obtain a numerical value for  $\sin \theta$ .

The constant  $\frac{1}{\sqrt{K'}} = \sqrt{\frac{n}{2\sigma}}$  is obtained from a knowledge of the conductivity of the ground as actually measured by the apparatus.

Taking  $\sigma = 10^8$  E.S.U. for Slough and  $n = 0.78 \times 10^6$  cycles per second for Bournemouth,

$$\frac{1}{\sqrt{K'}} = 0.062,$$

so that

$$\sin \theta = 0.062 \times \frac{Z - Z_0}{X - X_0} \times C_h$$

To proceed further, we must know  $Z$  and  $Z_0$  when  $X$  and  $X_0$  can be calculated.

$Z_0$  is the day value of the signal strength while  $Z$  is the value at the instant when  $\beta$  is measured.  $X$  is obtained from the equation  $X = Z \tan B$  and  $X_0$  is obtained from equation (6).

Unfortunately, the variation of both  $B$  and  $Z$  were too rapid to enable the value at any instant to be compared. In order to make this possible it would be necessary to take readings at the rate of 1 per 5 seconds simultaneously on both instruments. This was actually done in the case of  $Z$ , but the Hertzian rod operator could not take the reading more rapidly than once per half minute. In these circumstances the best that can be done is to assume that at a given value of  $B$  the value of  $Z$  did not exceed a certain maximum value ( $Z$  maximum), which can easily be fixed by taking the highest value of  $Z$  occurring during a few minutes on either side of the instant in question. In this case we get a maximum value for  $\theta$ , for it can be shown that

$$\sin \theta < 0.062 \cdot \frac{Z - Z_0}{X - X_0} \times C_h,$$

the value  $X$  being obtained on the assumption  $Z = Z$  maximum.

Under these conditions the values of  $B$  which leads to the smallest maximum value of  $\theta$  will be most interesting; so to make the calculation we shall naturally select the peak value of  $B$ . Intermediate values are of no particular interest.

The values of  $\theta_{\max}$  obtained by taking a random selection of peak values of  $B$  during the investigation are shown in Table III.

Table III.—Maximum Angle of Incidence calculated by Angle B and Intensity Z.

Date.	Time. G.M.T.	B degrees.	Z max.	$\theta_{\text{max.}}$ degrees.
28.5.25	1852½	6	16	38
28.5.25	2115	12	18	19
28.5.25	2052½	7	16	32
28.5.25	2120½	9	16	22
11.6.25	2111½	9.4	18	25
18.6.25	2023½	6	19	44
18.6.25	2026½	8	19	32
18.6.25	2056½	8	19	32
25.6.25	2103	7	20	38
25.6.25	2040	8	17	23

(b) *Tilting Coil Method (Angle F).*—The theoretical analysis shows that in this case the angle of inclination can be obtained from the relation (12)

$$\sin \theta = \gamma/\alpha \sqrt{K'} = \sqrt{K'} \tan F.$$

It is clear that to get a real positive value for  $\theta$  the conditions are

$$0 < F < \tan^{-1} 1/\sqrt{K'}$$

or  $0 < F < 3.5^\circ$

(under these conditions of wave-length and conductivity).

A glance at the curves of  $F$  (fig. 3) shows that this condition is fulfilled in the majority of cases, but that there are occasions when  $F$  becomes negative and also others when it becomes greater than  $3.5^\circ$ . The presence of these "impossible" values for  $F$  at once shows that we are not dealing with a single wave; the alternatives being either a small lateral deviation of the vertically polarised wave from the plane  $zOx$ , for which  $\alpha$  would then have a finite value, or the existence of at least two downcoming waves. Which of these two alternatives is the correct one must remain a matter of doubt until more accurate measurement of lateral deviation have been rendered possible. In either case it is quite impossible to obtain a value of  $\theta$  from these  $F$  curves alone, but in both cases, if we choose a moment when  $\alpha$  is large—say, of the same order as  $B_0$ —the chance of obtaining a false value for  $\theta$  becomes negligible. For since lateral deviation, if it exists, is small, a large value for  $\alpha$  means that the preponderating part of this component is produced by the downcoming wave, and hence will alone determine  $F$ , and the two or more waves, if they exist, must be combining (*i.e.* approximately in phase) when  $\alpha$  is large. Here again  $F$  will give a true value of  $\theta$  for the resultant downcoming wave.

Thus, to obtain  $F$  we must choose those instants when by inspection of the simultaneous curves of  $\alpha/Z$  and  $Z$  we see that  $\alpha$  is of the same order as  $\beta_0$ . If this is done, it is found that at periods of large  $\alpha$  the value of  $F$  tends to settle down to an average value of about  $2^\circ$  and has no "impossible" values.

From this we at once get

$$\sin \theta = \sqrt{K'} \tan F = 16.2 \times 0.035.$$

Hence

$$\theta = 34^\circ.$$

The accuracy of the result is largely dependent on the accuracy with which we know  $K'$ .

Although there is a remarkable tendency for the value of  $F$  to remain at about  $2^\circ$  it sometimes has other values when the value of  $\alpha/\beta_0$  is sufficiently large for a calculation to be made. A selection of such values has been made and the values of  $\theta$  calculated from them are given in Table IV, assuming  $\sigma = 10^8$ .

Table IV. —Calculation of  $\theta$  from Angle  $F$ . Assume  $\sigma = 10^8$ .

Date.	Time G.M.T.	$\alpha/\beta_0$	$F$ degrees.	$\theta$ degrees.	$E_1/E_0$ .
18.6.25	2107½	2	1.6	28	1.2
18.6.25	2111½	1	(0)*	(0)	0.5
18.6.25	2122½	1	2.0	34	0.6
18.6.25	2124	1	1.2	19	0.5
25.6.25	2045	0.5	2.0	34	0.3
25.6.25	2051½	0.5	(0)*	(0)	0.3
25.6.25	2112½	>2	1.0	16	>1.1
25.6.25	2113	>2	1.0	16	>1.1
25.6.25	2113½	>2	2.0	34	>1.2
25.6.25	2114	>2	2.0	34	>1.2

\* The accuracy of this method decreases very rapidly as  $F$  decreases to zero, and the values of  $\theta$  obtained in these two cases are probably due to this limitation.

In concluding this section it is to be observed that the calculation of  $\theta$  from the measurements of the angle " $F$ " refers only to the horizontally polarised portions of the downcoming waves. The other two methods, whose results are discussed in sub-sections (a) and (c), give the angle of incidence of the vertically polarised portion of the downcoming waves.

(c) *Loop-Aerial Method*.—The relation between the angle of incidence and the quantities measured by the loop-aerial and signal-strength apparatus is given by equation (17) of the theoretical analysis (section 5), viz. :—

$$\sin \theta = \left| \frac{Z - Z_0}{\beta - \beta_0} \right| \quad (17)$$

The ability to get a numerical value for  $\theta$  by this relation from the information contained in the  $\beta/Z$  and  $Z$  curves (*e.g.* fig. 9) depends first on whether variations were slow enough to enable corresponding values of  $\beta/Z$  and  $Z$  to be selected at any given instant; and secondly, on whether we can make any definite assumption with regard to the phase relationship of the two waves. As regards the first point, a close inspection of the curves shows that only in the case of the rapid tests (see fig. 10) is it possible to make sure of obtaining for a value of  $\beta/Z$  at a given instant the corresponding value of  $Z$  at the same instant. We can, however, utilise the slower tests in the same way as with the  $B$  curves to obtain maximum values of  $\theta$ . As regards the second point a careful consideration of the whole problem leads to the conclusion that it is safe to assume the direct wave and resultant downcoming wave are approximately in phase when both  $\beta/Z$  and  $Z$  have obtained peak values. This would not be possible but for the fact that a phase difference up to about  $60^\circ$  makes very little difference in the results. With this assumption we can treat the vector quantities in (17) as scalar quantities and thus obtain a numerical value for  $\theta$ .

The values of  $\theta$  for various instants during the rapid tests are given in Table V, while the following is an example of how the values were calculated and the possible error estimated:—

*Example.*—On June 25, 1925, at 2103.40'' (fig. 10).

$$Z = 19.7 \text{ and } \beta/Z = 1.68.$$

Therefore

$$\beta = 33.1.$$

From day curves of  $Z$  on same day

$$Z_0 = 11.5 \quad \beta_0 = 11.5.$$

The waves are approximately in phase as both  $Z$  and  $\beta/Z$  are at peak values.

$$\begin{aligned} \sin \theta &= \frac{Z - Z_0}{\beta - \beta_0} \\ &= \frac{8.2}{21.6} \end{aligned}$$

Hence

$$\theta = 22.5^\circ.$$

*Possible Errors.*—Assuming  $Z$  and  $\beta/Z$  can be measured to  $\pm 10$  per cent.—

Max. possible error in  $Z$  causes  $\pm 1.5^\circ$  change in  $\theta$ .

Max. possible error in  $\beta$  causes  $\pm 4.0^\circ$  change in  $\theta$ .



The waves are assumed to be in phase. It can be shown that large variations in phase have a small effect on the derived value of  $\theta$  for given values of  $Z$  and  $\beta/Z$ . For example, even if the phase difference was  $45^\circ$ ,  $\theta$  would only be increased by about  $1.5^\circ$ . The maximum possible error is, therefore, about  $\pm 6^\circ$  and the probable accuracy is far higher than this.

The values of  $\theta$  in Table V are more satisfactory than those of  $\theta_{\max}$  in Table III, as they are definite measurements of the angle of incidence of the resultant downcoming waves at each particular moment. The limiting values of  $\theta$  are, however, of sufficient interest to be worked out where no others are available. This has, therefore, been done in Table VI. The values of  $\theta_{\max}$ .

Table V. —Calculation of Angle of Incidence from  $\beta/Z$  and  $Z$  (Rapid Tests).

Date.	Time G.M.T.	$Z$ .	$\beta/Z$ .	$\theta$ degrees.	$E_1/E_0$ .
18.6.25	2030.00	17	1.6	21	0.7
18.6.25	2032.50	15.2	1.3	27	0.4
18.6.25	2034.40	16.5	1.4	25	0.6
18.6.25	2101.10	16.5	1.6	21	0.7
18.6.25	2104.05	20	1.9	19	1.2
18.6.25	2104.25	19.6	2.1	17	1.4
25.6.25	2030.00	14.8	1.4	21	0.4
25.6.25	2100.00	14.2	1.4	19	0.4
25.6.25	2103.40	19.7	1.7	23	1.1

are here obtained in the same way as those in Table III, for it can be shown in these cases that if a limiting value  $Z_{\max}$  be assigned to  $Z$ , and if  $Z_1 < Z_0$

$$\sin \theta < \frac{Z_{\max} - Z_0}{\beta - \beta_0},$$

where  $\beta$  is obtained from  $Z_{\max}$  by using  $\beta/Z$  as obtained from the curves.

Table VI. —Calculation of Maximum Angle of Incidence from  $\beta/Z$  Curves.

Date.	Time G.M.T.	$Z_{\max}$ .	$\beta/Z$ .	$\beta$ .	$\theta_{\max}$ degrees.
28.5.25	1912½	15	1.5	22	20
28.5.25	1916	20	1.7	33	23
28.5.25	2106	19	1.9	35	19
28.5.25	2112	17	2.1	36	13
28.5.25	2123	19	1.7	32	21
11.6.25	2107½	17	1.9	31	17
11.6.25	2118½	18	1.5	28	24
18.6.25	2030	19	1.5	29	27
18.6.25	2104	21	1.7	35	25
18.6.25	2117½	19	1.5	29	26
18.6.25	2112½	16	1.9	30	15
25.6.25	1843	11.7	1.1	13	15
25.6.25	2102	18	1.4	25	29
25.6.25	2112½	17	1.9	31	23

10. *Calculation of Ratio of Intensity of the Downcoming Wave to that of the Direct Wave.*  $E_1/E_0$ .

This ratio, in the case of vertically polarised waves, is obtained from the  $Z$  curves at any instant provided the angle of incidence is known at that instant. For at the peak values, where we assume the two waves are in phase, we have seen from section 5, equation (18),

$$\frac{E_1}{E_0} = \frac{Z - Z_0}{Z_0(1 + \rho_v) \sin \theta}.$$

Values for  $\rho_v$  obtained from equation (21) are given in Table VII.

In the case of the horizontally polarised waves the ratio of intensities is obtained from the value of  $\alpha$  at an instant when  $\theta$  is known. In order to obtain  $\alpha$  the value of  $Z$  must be found at a given value of  $\alpha/Z$ . The ratio  $E_1/E_0$  is thus calculated according to equation (20).

The values of  $\rho_h$  for various values of  $\theta$  are also given in Table VII.

Table VII.—Values of Reflection Ratio of the Earth's Surface for Vertically and Horizontally Polarised Waves for Various Angles of Incidence.  
( $\lambda = 386$  meters :  $\sigma = 10^8$  E.S.U.)

$\theta$ degrees.	$\rho_v$ .	$\rho_h$ .
0	0.92	0.92
10	0.92	0.92
30	0.91	0.93
45	0.89	0.93
60	0.84	0.97
70	0.78	0.98
80	0.62	0.99

The values of the intensity ratio have been worked out for the various instants recorded in Tables IV and V, and are inserted in the last column of these Tables. It is to be noticed from these Tables that the extreme values of  $E_1/E_0$  are of the same order for both the vertically and horizontally polarised waves.

11.—*Discussion of Results and Conclusions.*

In this section it will be as well to review briefly the experiments described in this paper, in order to obtain a clear idea of the position of the problem at the time of writing (September, 1925). In the first place the failure of the methods of measuring the directions of the electric and magnetic forces to give positive evidence of the receipt of downcoming wireless waves at the earth's surface

has been overcome by working on shorter wave-lengths. Operating on wave-lengths in the neighbourhood of 400 metres it has been shown that the directions of the component forces in the arriving waves can vary considerably from their normal daytime values. Such variations begin at times in the proximity of sunset or after total darkness prevails, and accompany the more commonly known variations in signal strength and apparent bearings as observed on a direction-finder. The magnitudes of the variations already observed on the two independent sets of apparatus are considered to provide direct evidence of the reception of wireless waves arriving at the earth's surface at a comparatively small angle of incidence (*e.g.*,  $30^\circ$  or less to the vertical); for although it may contribute to the result, the departure of the path of travel of the wave from the great-circle plane between transmitter and receiver is not alone sufficient to account for the results obtained. Further, from the fact that the variations in the direction of the forces are obtained both in the plane of propagation and at right angles thereto, it may be deduced that the downcoming waves can be polarised with the electric force in either a vertical or horizontal plane.

By combining the above measurements with simultaneous observations of the strength of the vertical electric force of the arriving waves, a means is provided of determining the angle of incidence of both the vertically and the horizontally polarised components of the downcoming waves. Typical results are given in the paper of such determinations which have been carried out at Slough on the transmissions from the Bournemouth Station, and these show that the resulting angles of incidence can have any value between the limits of  $16^\circ$  and  $34^\circ$ .

A third method of obtaining direct evidence of the existence of downcoming waves at night and of measuring their angle of incidence, is based upon the fact that in such cases the resultant electric and magnetic forces at the earth's surface are not equal as they would be for waves travelling horizontally. The results of such measurements carried out simultaneously with those mentioned above show that the angle of incidence may have any value from  $13^\circ$  to  $29^\circ$ . It must be remembered, in considering these results, first that in the experiments all the quantities under observation were varying over large ranges every few seconds, and secondly, that there is no reason to suppose that only a simple wave at a definite and steady angle of incidence is coming down. Indeed, evidence was provided among the observations of the reception of two or more downcoming waves at varying angles, and it is evident that in such cases only a sort of weighted mean angle of incidence can

be measured. Bearing in mind, then, that the numerical results represent at least the order of the angle of incidence, let us consider the limiting values of  $13^\circ$  and  $34^\circ$ .

If the last value represents the case of a simple wave which has been symmetrically reflected or deflected from the upper atmosphere in its passage from Bournemouth to Slough, the maximum height of this path becomes 55 miles or 88 kilometres. This is in good agreement with recent estimates of the height of the ionised deflecting layer for wave-lengths of the order employed; for example in experiments of Appleton and Barnett on the same wave-length, a value of 80-90 km. was obtained for this height (4), while Breit and Tuve (5), operating on a wave-length of 71.3 metres, have obtained experimental evidence for a deflecting layer at a height of 80 km. With regard to the other small angles of incidence recorded above, it is evident that if these also refer to a simple wave propagated in the above manner, the height at which the deflection occurred must be greater: the height being about three times the above values in order to secure an angle of incidence of  $13^\circ$  or less. Another manner of viewing the matter, however, takes account of the multiple reflection of waves from the upper atmosphere and the earth alternately. The values in Table VII show that the earth is a relatively good reflector for wave-lengths and angles of incidence of the order under consideration; and waves which have been deflected two, three and four times from the upper atmosphere would give angles of incidence of about  $19^\circ$ ,  $13^\circ$ , and  $10^\circ$  respectively. How important such multiple reflected waves are depends on their intensities relative to that of the main wave, and is one of the subjects that remains for future investigation.

Having obtained the angle of incidence, the experimental results also furnish data by which the relative intensities of the downcoming and direct waves may be determined. Some measurements in the paper have given values varying from 0.3 to 1.4 for this ratio, showing that under the conditions of those experiments the intensity of the downcoming wave can be of the same order as that of the direct wave. Under such conditions the "reflection coefficient" of the upper ionised layer can be estimated if the attenuation of the direct wave along the earth's surface is known. Unfortunately no experimental measurements of this quantity have so far been carried out in this country. By substituting the known value of the earth's conductivity in the theoretical formulæ given by Sommerfeld, a value of attenuation of the waves travelling from Bournemouth to Slough can be obtained. On such a basis, the "reflection coefficient" of the upper layer can be shown to be about 0.2.

Although in this general investigation, a few preliminary observations have

already been carried out at Slough on the transmissions from the Birmingham station ; there are insufficient definite results to record here. In the light of the experience gained, it is proposed to continue the investigation on the transmissions from Bournemouth and other stations operating on different wave-lengths and with different directions of transmission. It is hoped thereby to obtain further data and to improve the accuracy of the results so far obtained.

#### 12. *Acknowledgments.*

This work was carried out for the Radio Research Board under the Department of Scientific and Industrial Research, and the authors are indebted to the Committees on Directional Wireless and Propagation of Waves for their helpful criticism. The authors also wish to acknowledge the general assistance rendered by Mr. S. R. Chapman, M.Sc., throughout the investigation, and the help given by Messrs. E. L. Hatcher, G. W. Warren, A. C. Haxton and A. H. Free in connection with the large amount of simultaneous observation work carried out.

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*New Experiments upon the Combustion of Well-dried Carbon  
Monoxide and Oxygen Mixtures.—Part I.*

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*Introduction.*

In the year 1880, H. B. Dixon (in repeating Bunsen's experiments on the division of oxygen between carbon monoxide and hydrogen, when both are present in excess) discovered that a mixture of carbon monoxide and oxygen, dried by long contact with phosphoric anhydride, would not explode when sparked in the usual way in a eudiometer over mercury, although the presence of a trace either of moisture or of any gas containing hydrogen at once rendered the mixture explosive.\*

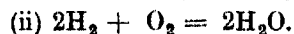
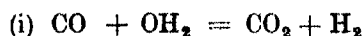
In 1883, H. B. Baker, working in Dixon's laboratory at Balliol College, Oxford, found that purified charcoal, when heated to redness in carefully dried oxygen, burned with extreme slowness and without flame, yielding principally the monoxide, the proportion of the dioxide formed varying inversely with the degree of dryness of the system. He also proved that highly purified sulphur or phosphorus may be repeatedly distilled in an apparatus filled with carefully dried oxygen, without any combustion occurring, although the admission of a mere trace of moisture immediately caused a vivid burning. In subsequent years Baker proved that a large number of gaseous interactions are at least greatly assisted, if they are not actually conditioned, by the presence of moisture. Thus, (1) a mixture of hydrogen and chlorine, well dried by long contact with phosphoric anhydride, does not explode on exposure to sunlight as does an undried one; (2) ammonia and hydrogen chloride, when similarly dried, do not combine when mixed in the cold; whilst (3) thoroughly dried electrolytic gas, free from hydrocarbon impurity, may be heated to redness, or exposed to ultra-violet light, without any measurable formation of water occurring. Such experiments undoubtedly proved that the removal of moisture from certain gaseous systems increases in an extraordinary degree their resistance to chemical change, although they can hardly

\* 'British Association Reports,' p. 503 (1880); 'Phil. Trans.,' vol. 175, p. 617 (1884).

be said to have proved, as is sometimes supposed, that the presence of moisture is *absolutely essential* to chemical change in such cases.

How exceedingly small is the amount of moisture which "makes all the difference" in the cases just cited may be gathered from an estimate made many years ago by E. W. Morley that the mere passing of a gas slowly through a long column of phosphoric anhydride leaves only 3 milligrams of water-vapour per million litres (*i.e.*, less than 4 molecules of steam per 1000 million molecules of gas)\*; yet a much more prolonged drying is usually considered necessary to demonstrate the comparative inertness of two gases which in the presence of moisture would combine quite readily. This, indeed, has always constituted a great difficulty in the way of explaining from a kinetic standpoint how the water really functions in such cases.

The subject has naturally attracted much attention, because of its fundamental interest, and various explanations of the function of water have been put forward at various times. For some years after Dixon's discovery in regard to carbon monoxide, purely chemical explanations, involving the idea that steam molecules act as "carriers of oxygen" to the combustible gas, were most in favour. Thus Dixon supposed that, in the ordinary combustion of carbon monoxide, the steam acts catalytically,† as follows:—



It may here be observed that in his Bakerian Lecture upon "The Rate of Explosion of Gases" (1893) Dixon expressed the opinion, that "*at the extreme temperature of the explosion wave, as well as in ordinary combustion, carbonic oxide is oxidised by the steam and not directly by the oxygen.*"‡ Moritz Traube (in 1885) and Mendeljeff (in 1891) put forward modifications of Dixon's view postulating the intermediate formation of hydrogen peroxide during the combustion of carbon monoxide; both of them, however, agreed that in flames and explosions carbon monoxide is always indirectly oxidised through the medium of steam and/or hydrogen peroxide.

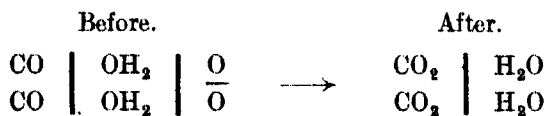
H. E. Armstrong, who always contends that chemical interactions cannot occur between two perfectly pure substances, but require the conjunction of an electrolyte to form "a closed conducting circuit," supposed that the presence of steam, which he regards as being rendered conducting by

\* 'Amer. Journ. Sci.,' vol. 34, p. 199 (1887), and 'J. Amer. C. S.,' vol. 26, p. 1171 (1904).

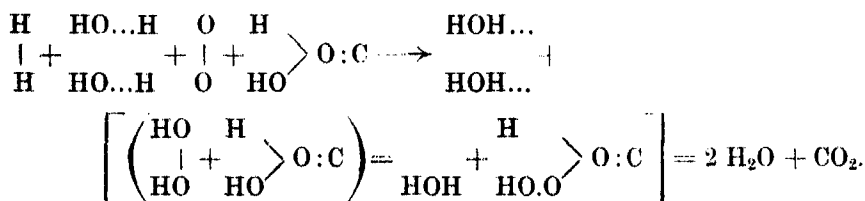
† 'Phil. Trans.,' Part II, p. 617 (1884).

‡ 'Phil. Trans.,' A, p. 112 (1893).

association with some traces of an electrolyte impurity, provides the necessary conditions for the passage of the current, the oxygen playing the part of depolariser,\* thus :—



According to this view, CO and O<sub>2</sub> molecules are absolutely inert towards each other. Indeed, quite recently, Armstrong declared carbon monoxide to be "*per se* an incombustible gas," adding that "*an explanation may be found in the assumption that when a moist carbon monoxide mixture is sparked or fired, some hydrone is decomposed and sufficient hydrogen set free to act in a 'depolarising' circuit together with the oxide, as thus*"† :—



This is perhaps the most elaborate form which any chemical explanation has hitherto taken. although all of them involve the assumption that in the combustion of carbon monoxide *steam is continuously decomposed and regenerated*.

As far back as 1886, however, Lothar Meyer, in repeating H. B. Dixon's original experiments, found that a mixture of  $2\text{CO} + \text{O}_2$ , which had been dried by contact with phosphoric anhydride for 6 days in a eudiometer over mercury, and which was not ignited at 156 mm. pressure by a Rhumkorff spark of low intensity, could be made to combine by passing through it a much more powerful spark continuously for two minutes, combustion being complete.‡ This led him to put forward the view that a far higher temperature is required to initiate the interaction between carbon monoxide and oxygen than that between carbon monoxide and steam; so that whereas the latter reaction is easily initiated by a spark of low intensity, the former requires one of high

\* 'Trans. Chem. Soc.,' vol. 49, p. 112 (1886).

† 'Roy. Soc. Proc.,' B, vol. 98, pp. 202-206 (1925).

‡ 'Berichte deut. Chem. Ges.,' vol. 19, p. 1099 (1886).



intensity. Probably the degree of dryness attained in his experiments would not be considered to-day sufficient to decide such a point; but the experiments which will be hereinafter described show that his conclusion was perhaps nearer the mark than has been generally credited.

As time went on, other significant facts were discovered which tended to throw doubt upon the extreme doctrine that carbon monoxide and oxygen are in *all circumstances* mutually inert and incapable of combining directly. Indeed, as early as in 1886, Dixon had observed that "*in the explosion of cyanogen with an excess of oxygen, the formation of carbonic acid is complete, and is not affected by the presence of moisture.*" Ten years later, in conjunction with Strange and Graham, he found that, contrary to expectations, the flame produced by the explosion of a well-dried mixture of cyanogen with twice its own volume of oxygen, when analysed photographically upon a rapidly-moving film, "does not appear to differ from the flame given by the same gases mixed with 1.5 per cent. of water." From which observations he concluded that "*in a mixture of freshly-formed carbon monoxide and oxygen, these gases unite as the mass cools down without the intervention of steam; and where steam is present it does not appreciably alter the time during which the change continues.*"\* In this connection also it may be recalled how, when in 1894 Smithells and Dent examined in their "separator" the flame of a  $P_2O_5$ -dried mixture of cyanogen with sufficient air to give a separation of the two cones, they found that, when the cones were widely separated, the upper one, in which the combustion was almost wholly that of carbon monoxide to dioxide, was immediately extinguished by bringing a bottle of dry air over it; but that "on approximating the two cones a point was soon reached, where it was impossible any longer to extinguish the outer cone by such means."† This experiment certainly suggests that carbon monoxide will combine directly with oxygen, provided that it is freshly formed in a flame, and presumably in an "ionised" condition.

In 1903,‡ A. F. Girvan describing certain experiments which he had made to see whether the drying of an explosive mixture of carbon monoxide and oxygen by exposure to low temperature, produced by either liquid air or solid carbon dioxide in alcohol, would be sufficient to prevent chemical union

\* 'Trans. Chem. Soc.,' vol. 69, p. 773 (1896).

† 'Trans. Chem. Soc.,' vol. 65, p. 610 (1893).

‡ 'Proc. Chem. Soc.,' vol. 19, pp. 236-238 (1903); unfortunately, no fuller account of these interesting experiments appears to have been published.

taking place when the gas was sparked after it had regained the ordinary temperature. He found that, whereas a series of "powerful sparks" from an induction coil would not ignite a mixture which had been dried at either  $-180^{\circ}$  or  $-80^{\circ}$  C., they would always do so when the mixture had been dried at a temperature between  $-50^{\circ}$  and  $-35^{\circ}$  C., whilst a single spark would always cause an explosion if the drying had been at  $-15^{\circ}$  C. only. He also remarked that "the explosion produced by powerful sparks in the gases dried between  $-50^{\circ}$  and  $-35^{\circ}$  is of a very different character from that obtained with the wet gases; the latter is very quick and violent, and gives a metallic click, but the former takes place quietly, and the explosive wave travels quite slowly along the tube."

In 1923, one of us (W.A.B.), in conjunction with D. M. Newitt and D. T. A. Townend, described to the Chemical Society some experiments upon "The Relative Influence of Water Vapour and Hydrogen upon the Explosion of Carbon Monoxide-Air Mixtures at High Pressures" \* in which it was shown that the presence or otherwise of water vapour has very little influence upon the rate of pressure-development in the explosion of a  $2\text{CO} + \text{O}_2 + 4\text{N}_2$  mixture at an initial pressure of 50 atmospheres, as the following results indicate :—

Hygroscopic State of Gases in Explosion Chamber.	Time Taken	Maximum	Per cent.
	for Attain-	Pressure	Pressure
	ment of Maximum Pressure. Secs.	Developed. Atmos.	Fall in 0.5 secs. after $P_m$ .
Series { (1) $\text{P}_2\text{O}_5$ -dried .....	0.18	400	9
(2) Undried .....	0.15	411	10
(3) Moist .....	0.19	395	11.5

H. B. Dixon pointed out to us in a private communication (8/9/23) that if (as we believe) the "dryness" of the bomb in the foregoing series (1) could be relied upon, "it would seem that CO combines directly with  $\text{O}_2$  at high pressures." This possibility had already suggested itself to our minds as the outcome of a preliminary study of the flame-spectrum of carbon monoxide, whose extension far into the ultra-violet must (as we said) "surely be due to the formation of molecules (or complexes) in a much more highly vibratory

\* 'Trans. Chem. Soc.,' vol. 123, pp. 2008-2021 (1923); *ibid.*, p. 2020.

state than would be likely to arise merely by interaction between CO and OH<sub>2</sub> molecules."

Moreover, in two papers upon "The Flame Spectra of Carbon Monoxide and Water Gas,"\* which one of us (F.R.W.) has recently communicated to the Society, is afforded, what H. B. Dixon agrees to be, "the first clear evidence that in an ordinary CO flame both the direct and indirect actions are going on at once," to quote (with his permission) from a further private communication from him on the subject.†

The new evidence which is submitted in this and the succeeding papers comprises four independent sets of experiments, namely :—

- (A) Showing the effect of progressive "drying" upon the minimum "spark-energy" required to ignite a 2CO + O<sub>2</sub> mixture at atmospheric pressure.
- (B) Showing that a six-months P<sub>2</sub>O<sub>5</sub>-dried 2CO + O<sub>2</sub> mixture may be exploded at atmospheric pressure by a sufficiently powerful condenser discharge.
- (C) Showing the influence of pressure upon the ignitibility of P<sub>2</sub>O<sub>5</sub>-dried 2CO + O<sub>2</sub> mixtures by means of sparks of ordinary intensity.
- (D) Spectrogram of a well-dried CO-air explosion flame at an initial pressure of 25 atmospheres, showing the absence of steam lines.

#### EXPERIMENTAL.

- (A) *Showing the Effect of Progressive "Drying" upon the Minimum Condenser Discharge Spark-Energy required to Ignite a 2CO + O<sub>2</sub> Mixture at Atmospheric Pressure.*

Some years ago, in a series of papers,‡ Prof. W. M. Thornton showed that, for given sparking conditions (*e.g.*, electrodes, type of discharge, voltage, etc.), a certain minimum spark energy is required to ignite a given explosive gaseous mixture; and, in studying the igniting powers of condenser-discharge sparks, which are oscillatory and of extremely short duration, and start with

\* 'Roy. Soc. Proc.,' A, vol. 100, pp. 176-186 and 523-526 (1925).

† He also added, "I have long been sure that CO can unite directly with oxygen—as it does in the cyanogen reaction where the CO is the first product, and as it must do largely in your high-pressure explosions" (November 17, 1925).

‡ 'Roy. Soc. Proc.,' A, vol. 90, pp. 272-297 (1914); vol. 91, pp. 17-22 (1914); vol. 92, pp. 9-22 and 381-401 (1915-16).

ionisation of the gas between the poles, he proved that "there is in every case a well-marked limit to their igniting power." Thus, in the case of a CO-air mixture containing 30 per cent. of the combustible gas, he found that with a 100-volt condenser discharge a minimum capacity of 2.0 microfarads was required for ignition.

It seemed to us that, if the presence of water vapour has any material influence upon the ignitibility of a given explosive mixture of carbon monoxide and oxygen (say  $2\text{CO} + \text{O}_2$ ), then the minimum condenser-discharge-spark-energy required to ignite it should vary according to the amount of water vapour present; so that, on progressively drying such a mixture from a condition of (say) "saturation" at room temperature to one which is in equilibrium with a fairly efficient drying agent, as, for example, freshly-ignited calcium chloride, the minimum spark-energy required for ignition should progressively increase, until at length it becomes many times greater than it ordinarily is.

On putting the matter to the test of experiment our anticipation proved to be correct, the minimum spark energy required to ignite a calcium-chloride-dried  $2\text{CO} + \text{O}_2$  mixture being some thirty times greater than for the same mixture when saturated with water vapour at the room temperature. Our experimental procedure was briefly as follows, the general arrangement of the apparatus employed being shown in fig. 1.

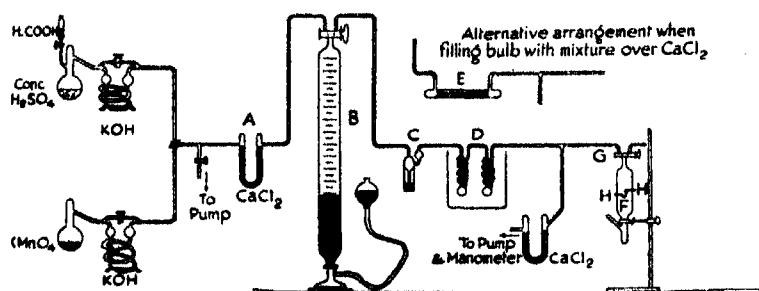


FIG. 1.

A mixture of pure carbon monoxide (2 vols.) and oxygen (1 vol.), prepared as will be described in the next section hereof, was made over clean re-distilled mercury in a graduated gas burette, B, each gas having been previously dried by passage through a U-tube A, containing calcium chloride. From this burette the mixture, whose composition had been accurately adjusted to  $2\text{CO} + \text{O}_2$  and verified by analysis, was slowly passed through *either* (a) a

bubbler C, containing ammonia-free distilled water at the room temperature, followed by two worms D, immersed in either ice or some freezing mixture at a definite temperature, or (b) a long tube E, packed with small pieces of calcium chloride, which had previously been ignited at  $300^{\circ}$  C., whereby its pressure of water vapour at room temperature had been reduced to as low as 0.25 mm. From such a "drying" system, the mixture was then allowed to pass very slowly into an exhausted explosion vessel F, similar to the one described in the next section hereof (fig. 4, *q.v.*), *except that* it was fitted at the top with a two-way glass tap G, lubricated with syrupy phosphoric acid, and with 1 mm. diameter platinum electrodes HH. The interior of the explosion vessel F (capacity  $\approx$  about 100 c.c.) had been previously thoroughly cleaned out successively with hot chromic-sulphuric acid, ammonia-free distilled water, etc. (as will be described in the next section hereof), and finally dried out by being strongly heated in a current of dust-free air dried by passage over well-ignited calcium chloride. Also, when experimenting with calcium-chloride-dried  $2\text{CO} + \text{O}_2$  mixtures, some of this drying agent was introduced through the side tube into the lower part of the explosion vessel.

In determining the minimum condenser discharge spark energy required to ignite the  $2\text{CO} + \text{O}_2$  mixture in varying hygroscopic states, a number of condensers of known capacity, which had been previously calibrated by means of a ballistic galvanometer and a 1 microfarad standard condenser, were charged from the mains up to 110 volts, as verified by an electrostatic voltmeter. The condensers were connected up with the electrodes of the explosion vessel through the double-pole double-throw switch S, as shown in fig. 5; and by gently tilting the explosion vessel the gap between the electrodes was reduced until the condenser discharged across it.

To begin with, a capacity was used well below that required to ignite the particular mixture under investigation, and a trial made. The capacity was then gradually increased, in steps of 0.1 or 0.25 microfarad, until a point was reached at which the mixture was fired by the discharge-spark. Three trials were given at each successive capacity before increasing it; and whenever several trials were necessary before reaching the "limiting" capacity, a special redetermination of the latter was made. Every precaution was taken to keep the electrodes perfectly clean throughout a given series of experiments; indeed, the whole elaborate cleaning operation previously referred to was repeated after every three or four ignitions. The results obtained were as follows:—

	Hygroscopic Condition of 2CO + O <sub>2</sub> Mixture.		Minimum Igniting Capacity at 110 volts Micro- farads.	Energy of Minimum Igniting Spark. $\Sigma = \frac{1}{2} cv^2$ = Joules $\times 10^6$
	Saturated with aq. Vapour at °C.	Per cent H <sub>2</sub> O by Volume Present.		
Mixture "saturated" at room tempera- ture	17.4°	2.00	0.76	4,600
	17.0°	1.98		
	14.5°	1.70	0.83	5,020
	14.0°	1.60	0.98	5,930
Mixture "saturated" at a low temperature controlled by ice or some freezing mix- ture	4.0°	0.80	4.00	24,200
	0.00°	0.60	4.80	29,040
	— 5°	0.40	8.00	48,400
	— 10°	0.26	10.07	60,900
	— 16°	0.16	17.25	104,350
	— 25°	0.06	18.79	113,800
Mixture .....	CaCl <sub>2</sub> dried	0.03	20.83	126,000

The results, which are plotted on the graph shown in fig. 2, are all seen to fall very near to a smooth curve. They prove that as the water vapour is

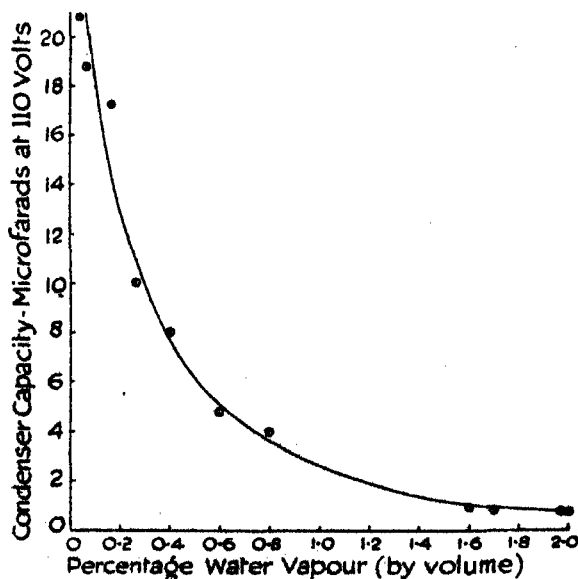


FIG. 2.—Ignition Energies (Condenser Discharge Sparks) for 2CO + O<sub>2</sub> mixtures. Under varying hygroscopic conditions.

progressively removed from a  $2\text{CO} + \text{O}_2$  mixture, its ignitibility by condenser discharge sparks rapidly diminishes, the minimum spark energy necessary to fire it increasing until with a calcium chloride-dried mixture it becomes something between twenty and thirty-fold as great as that required to ignite the same mixture when "saturated" with moisture at the room temperature (14 to  $17.5^\circ \text{C}$ .).

It is known that the discharge of a condenser, by bringing together wires attached to its terminals, is characterised by extreme rapidity, the first oscillation being completed in less than a millionth of a second. Its effects are certainly "impulsive"; the spark starts with collision-ionisation of the gas between the poles, which rises to a maximum in the first oscillation. Presumably it also has a high temperature, and gives rise to high local gas pressure, as is evident from the sharp crackling sound emitted. And if, as many authorities suppose, its igniting effect is probably an "ionising" one, the foregoing experiments would seem to indicate that the progressive drying of a  $2\text{CO} + \text{O}_2$  mixture necessitates an increasingly powerful "ionising" spark for its ignition; and they would explain the observations made by Lothar Meyer in 1886, and by A. F. Girvan in 1903, to which reference has already been made.

In this connection it may be mentioned that recently experiments have been made by Capt. G. I. Finch in these laboratories in which a direct current arc was maintained in  $\text{H}_2\text{SO}_4$ -dried pure electrolytic gas at various pressures between 30 and 150 mm., in which circumstances slow (non-explosive) combustion took place. The rate of combination was proportionate to the current, and independent of the voltage; from which it may be inferred that "ionisation" is the determining factor in such combinations.

(B) *Showing that a six-months  $\text{P}_2\text{O}_5$ -dried  $2\text{CO} + \text{O}_2$  Mixture can be exploded at Atmospheric Pressure by a sufficiently Powerful Condenser Discharge.*

The next step in our experimental enquiry was to ascertain whether or not an explosive  $2\text{CO} + \text{O}_2$  mixture which had been still more effectively dried by prolonged exposure to phosphoric anhydride, in accordance with "Bakerian" procedure, can be exploded by a sufficiently powerful condenser discharge. For this purpose, it was necessary to adopt special precautions in order to ensure, not only the utmost cleanliness in the explosion vessels used, but also the most efficient drying possible of the gaseous mixture. Our procedure will now be described in detail.

*Preparation and Drying of the Gaseous Mixtures.*—The apparatus employed

for preparing, purifying, mixing, and initially drying the two gases is shown diagrammatically in fig. 3. It was in one piece throughout; all joints in it were

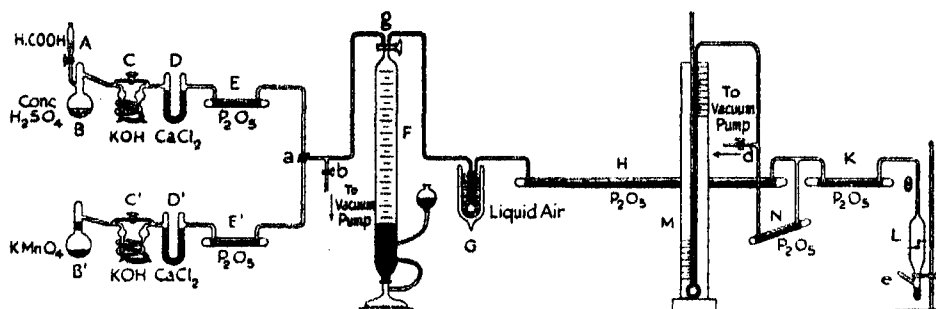


FIG. 3.—Apparatus for Preparation and Drying of  $2\text{CO} + \text{O}_2$  Mixtures.

of fused glass, the air blast of the blowpipe used for making them being “filtered” free from dust, and that used in blowing being calcium-chloride-dried. All stop-cocks in it were of glass, and lubricated with phosphoric acid produced by exposing its pure redistilled anhydride to the atmosphere for a few minutes. The mercury used in the gas-mixing burette, F, had previously been cleaned and redistilled *in vacuo*. All the component glass parts of the apparatus had been thoroughly cleaned out successively with (i) hot chromic-sulphuric acid mixture, and (ii) ammonia-free distilled water, before being dried in a current of hot dry dust-free air as will be described later.

The carbon monoxide was prepared by dropping pure re-distilled formic acid\* from the tap-funnel A into arsenic-free, pure re-distilled sulphuric acid\* in the flask B, gently warmed from without so as to give a slow, steady evolution of the gas, which then passed in succession through (i) the worm C, containing a strong solution of potassium hydroxide, (ii) the U-tube D, containing pieces of ignited calcium chloride, and (iii) the tube E, containing pure re-distilled phosphoric anhydride.

The oxygen was prepared by gently heating pure re-crystallised potassium permanganate in the flask B, and it was passed through a similar series of washing and drying tubes, C', D' and E', as shown in the diagram. Before preparing the gases, the whole of the apparatus to the left of the gas-burette F was exhausted through the tap b by a Hyvac pump.

The purified dry gases were collected and mixed over dry, clean, and re-distilled mercury in the gas burette F, each mixture being made to correspond

\* The freedom of each of these acids from arsenic was specially ascertained by applying Marsh's test.



as nearly as possible to the composition  $2\text{CO} + \text{O}_2$  (which was always verified by analysis), care being taken that any deviation therefrom should be in the direction of a slight excess of oxygen. Explosion analyses of the mixtures showed a ratio  $\text{C/A} = 0.50$ , as would be given by pure carbon monoxide, and that their nitrogen contents were always less than 1 per cent.

The following procedure was followed in transferring the gaseous mixture from the gas burette F to the explosion vessel L. The whole of the apparatus to the right of F was, first of all, thoroughly exhausted down to 0.01 mm. through the tap *d* by means of a Hyvac pump, which was kept continuously running for at least 24 hours, and in some cases for three or four days. During this period the explosion vessel was several times strongly heated externally with a naked bunsen flame to ensure the removal, as far as possible, of any moisture film still adhering to its walls. Finally, the tap *d* having been closed, the gaseous mixture was very slowly passed, at a rate between 0.5 and 1 c.c. per minute, from the gas burette F, through the drying system to the right thereof, into the explosion vessel L. This drying system comprised (i) a glass spiral G immersed in a bath of liquid air, and (ii) two tubes H and K, altogether 100 cm. long, filled with pure re-distilled phosphoric anhydride. Also, a quantity of similarly purified phosphoric anhydride had been previously introduced into the lower part of the explosion vessel L through its side tube *e*. As soon as the manometer M, which was connected with the system through the  $\text{P}_2\text{O}_5$ -filled guard-tube N, indicated that the explosion vessel L was full of the gaseous mixture at a pressure of about 10 mm. below the barometric at the time, a blowpipe flame was applied at the constriction  $\theta$ , previously made in the glass capillary leading into the explosion vessel, and its contents sealed off in the usual manner.

Four such explosion vessels, each of about 100 c.c. capacity and containing pure re-distilled phosphoric anhydride in their lower limbs, having thus been filled with the liquid-air and  $\text{P}_2\text{O}_5$ -dried  $2\text{CO} + \text{O}_2$  mixture at the room temperature, and a pressure of about 740 mm., each was put aside in a dark place for a period of six months, in order to ensure as complete a drying of the gaseous mixture as possible in contact with the phosphoric anhydride. During this "drying period" the lower limb of each vessel was frequently tapped in order to expose a fresh  $\text{P}_2\text{O}_5$  surface to the gaseous mixture. Also, once every fortnight all parts of each vessel down to the side tube were externally heated to about  $175^\circ\text{C}$ . by means of a specially designed electric heater, in order to disperse and get rid of any "moisture-film" adhering to the inner walls, care being taken to screen the  $\text{P}_2\text{O}_5$  in the lower limb from the effects of the heating.

*Preparation of the Phosphoric Anhydride Used.*—The phosphoric anhydride used had been specially prepared and purified by re-distilling it in a current of dry oxygen at  $800^{\circ}\text{C}$ . through a red-hot iron tube, according to a method devised by G. I. Finch and R. P. Fraser, a description of which has been separately published by them.\* It yields a voluminous crystalline product, entirely free from lower oxides of phosphorus, organic impurities, iron, etc.,† and of minimum vapour pressure, eminently suitable for the attainment of "Bakerian" dryness in gaseous systems. And throughout the whole of the long period covered by our experiments, it maintains unimpaired its pristine dry snow-like appearance, both in the main part of the drying system (i.e., the tubes, H, K, and N) and in the lower limbs of the four explosion vessels.

*Preparation of the Explosion Vessels.*—The form of explosion vessel (each about 100 c.c. capacity) used is shown in fig. 4, which is drawn to scale. One of the four such vessels used was made out of Jena "red-line resistance glass," and fitted with 2 mm. diameter platinum electrodes terminating in 5 mm. diameter platinum balls; the other three were likewise made out of a "high-resistance" glass, as "hard" in quality as could be used for the sealing-in of the platinum electrodes, which in these cases terminated in 3 mm. diameter balls. The dimensions of the various parts are shown in the diagram.

The *cleaning* of the interior of each vessel was carried out as follows:—It was first of all heated for at least 24 hours in a bath of strong chromic-sulphuric acid mixture, and then thoroughly washed out with "ammonia-free" distilled water and dried in a current of hot and dry "filtered" air. The vessel was then evacuated to approximately 0.01 mm., and the platinum electrodes "glowed out" electrically *in vacuo* for altogether about eight hours over a period of two days, in order to remove from them any occluded hydrogen, etc.

Then followed a second cleansing for another 24 hours with hot chromic-sulphuric acid mixture, carried out as before, after which the vessel was thoroughly washed out with several litres of hot "ammonia-free" distilled

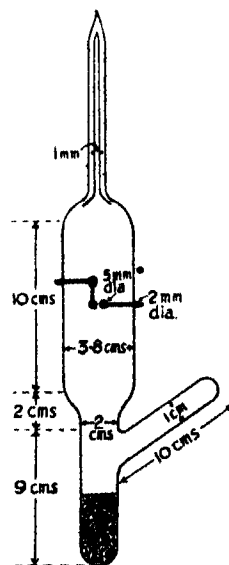


FIG. 4.—Explosion Vessel.

\* 'J. Chem. Soc.,' p. 117 (1926).

† The entire absence of all such impurities was ascertained by actual qualitative tests which need not be detailed.

water. Finally, the vessel was "steamed out" continuously for several hours by steam from boiling "ammonia-free" distilled water.

The *drying* of each vessel was subsequently accomplished in the following manner:—First of all, it was heated out at  $200^{\circ}\text{C}$ . for some hours in a current of dry air, which, after being confined in a holder over dilute sulphuric acid, was passed through a series of tubes containing (i) cotton wool, (ii) soda-lime, (iii) calcium chloride, and (iv) re-distilled phosphoric anhydride, before entering the heated explosion vessel, all joints in the apparatus being of fused glass. Next, the vessel, while still hot, was kept evacuated at  $0.01\text{ mm}$ . during several hours continuously, by means of a Hyvac pump, the platinum electrodes being again glowed out electrically in order to free them from any adherent "moisture film." Subsequently, the whole system was allowed to cool down to the room temperature in a current of dry filtered air, admitted through the aforesaid drying-train. Pure re-distilled phosphoric anhydride was then introduced into the lower part of the explosion vessel, through the side tube *e*, which was then sealed off. And, finally, the vertical  $1\text{ mm}$ . bore tube of the vessel was sealed on to the main apparatus (fig. 3), where it was kept continuously evacuated down to  $0.01\text{ mm}$ . for a period of 72 to 96 hours, during which it was frequently strongly heated by the external application of a bunsen flame, before being filled with the dry  $2\text{CO} + \text{O}_2$  mixture, as already described.

*The Arrangements for Sparking the  $\text{P}_2\text{O}_5$ -dried  $2\text{CO} + \text{O}_2$  Mixtures.*—The ignitibility of each of the six months  $\text{P}_2\text{O}_5$ -dried  $2\text{CO} + \text{O}_2$  mixtures, by means of a discharge at 970 volts from a condenser of known capacity, was tested in the following manner:—

The firing arrangements, which Capt. G. I. Finch kindly designed and supervised for us, are shown diagrammatically in fig. 5. The rotary converter, G,

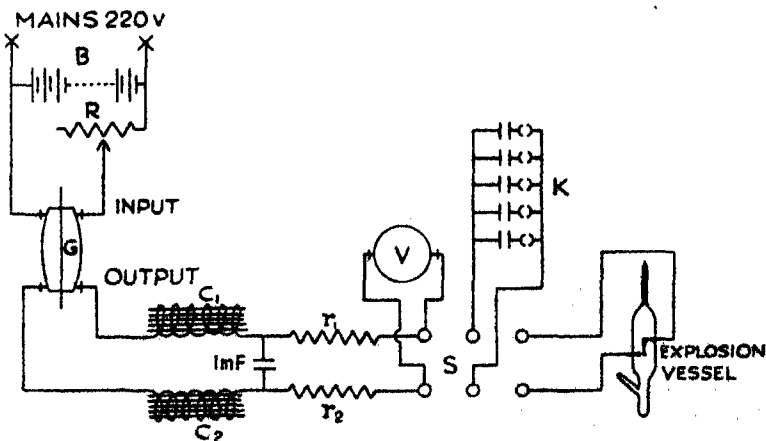


FIG. 5.

transformed the 220 volt supply from the mains up to a potential of 970 volts at which the firing condenser was charged; the floating accumulator battery, B, steadied the mains pressure. The speed of the generator, G, and hence the pressure of the high-tension output current, was controlled by the resistance, R. The normal speed of the generator was 3000 r.p.m., and its output commutator had 64 segments. A revolving mirror examination of the high tension arc discharge in air at a low-pressure revealed the presence of commutator ripple, and a few irregular fluctuations in the output pressure, due probably to slight sparking at the output brushes. It was, therefore, necessary to smooth the output current. This was satisfactorily achieved by passing the current through the two iron core chokes,  $C_1$  and  $C_2$ , the inductance and resistance of each being 55 henrys and 9000 ohms, respectively, shunting a 1 m.f. condenser across the output terminals of these, and, finally, through the resistances,  $r_1$  and  $r_2$ , of 80,000 ohms each, to one pair of terminals of the double-pole double-throw switch, S. A re-examination, by means of the revolving mirror, showed the discharge now to be perfectly smooth. The electrostatic voltmeter, V, was shunted across the aforesaid terminals; the middle terminals of this switch were connected to the standard plug-in condenser K, the total capacity of which was 7 microfarads, variable in steps of 0.01 microfarad. The third pair of terminals of the switch were connected by short, heavy multiple-strand copper leads to the variable spark gap of the explosion vessel. After the firing condenser had been charged up to 970 volts, the switch, S, was reversed, and by tilting the explosion vessel, the spark gap was reduced until the condenser discharged across it.

*The Explosion of the Six Months  $P_2O_5$ -dried  $2CO + O_2$  Mixtures.*—Altogether, four bulbs containing  $P_2O_5$ -dried  $2CO + O_2$  mixtures were prepared in the manner just described, and after a six-months' drying period, their ignitibilities by the said condenser discharge were tested. The general result was that, whereas ignition could not be effected with a condenser capacity of 0.5 microfarad, i.e., with a "spark energy" of less than about 0.235 Joule, at the aforesaid voltage, it always occurred instantly, and at first shot, with a condenser capacity of 0.77 microfarad or more, i.e., a spark energy of 0.362 Joule, or more.

Some idea of how powerful a spark was needed to ignite the mixtures may be gathered from the estimate of Captain Finch, who was in charge of the firing arrangements, that in the circuit employed, the peak current of the first oscillation of the discharge spark from a 0.75 microfarad condenser at 970 volts would be certainly not less than 700 amperes, and possibly many

times more. Moreover, it should be stated that when the discharge from a 0.5 microfarad condenser failed to ignite the mixtures, the spark simply passed across the gap between the electrodes without any sign whatever of a "halo" or such-like appearance.

*In all four cases, with a spark energy of 0.362 Joule or more, the mixture was instantly ignited at first shot, the resulting explosion spreading with a brilliant flame fairly rapidly through the containing vessel.* Judging, however, from sound and appearance, the explosions never seemed to be quite so "sharp" as they were in similar bulbs with an "undried" or a "CaCl<sub>2</sub>-dried" 2CO + O<sub>2</sub> mixture; and the combustion was never, in fact, quite complete, there always being a small residue of uncombined combustible mixture left.

The explosion of No. 1 mixture was effected at first shot with a "spark energy" of 0.47 Joule (1 microfarad at 970 volts) after two previous failures, at several hours intervals, with "spark energies" of 0.052 and 0.235 Joule (0.11 and 0.5 microfarad at 970 volts respectively). The flame spread throughout the mixture more rapidly than the eye could follow, the powdery, phosphoric anhydride in the lower part of the vessel being violently thrown up by the explosion, some of it as high as the electrodes. Subsequent analysis of the products showed that the combustion had been 77.2 per cent. complete.

The explosion of No. 2 mixture, which was effected at first shot with a "spark energy" of 0.94 Joule (2 microfarads at 970 volts), was witnessed by Professors H. E. Armstrong, A. Smithells, Sir Robert Robertson, and others; that of No. 3 mixture was carried out in the presence of Professor H. B. Baker at first shot with a "spark energy" of 2.35 Joules. In each of these cases, a brilliant flame quickly filled the vessel, and subsequent analysis of the products showed the combustion to have been about 88 per cent. complete.

The explosion of No. 4 mixture was effected at first shot with a "spark energy" of 0.362 Joule (0.75 microfarad at 970 volts) after a previous failure three days before with a "spark energy" of 0.235 Joule only (0.5 microfarad at 970 volts). The flame spread rapidly throughout the mixture, and a photograph of the explosion (which is reproduced in fig. 6) showed that it had completely filled the vessel. Subsequent analysis of the products showed the combustion to have been about 74.3 per cent. complete. Full particulars of these experiments are set out in Table I.

It would thus appear that the minimum condenser "spark energy," at 970 volts, required to ignite such P<sub>2</sub>O<sub>5</sub>-dried mixtures as the foregoing, probably lies somewhere between 0.235 and 0.362 Joule. It is also evident that, at such extreme dryness, even when the "spark energy" is sufficient to ignite

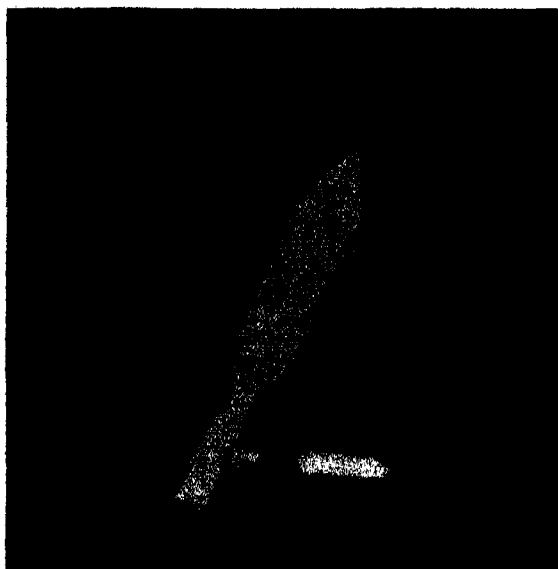


FIG. 6.

the gaseous mixture, and the resulting flame spreads rapidly throughout it, its resistance to combustion is still so great that an appreciable amount of it remains unburnt. Thus it was always noticed that the explosions were comparatively "soft" ones, no "click" being audible in any of them; and the incompleteness of the combustions indicated a "reluctance to burn" as though the flame was rather deficient in self-igniting power.

Attention is directed to the fact that in the four experiments under consideration, the greater the energy (up to a limit) of the spark which ignited the mixture, the more complete was the combustion in the subsequent explosion, thus :—

Energy of the Spark Causing Ignition Joule.	Percentage Combustion.
0.362	74.3
0.47	77.2
0.94 } 2.35 }	88 approx.

In this connection it may be mentioned that in some similar comparative experiments where the  $2\text{CO} + \text{O}_2$  mixtures had been dried for one or two weeks in contact with well-ignited calcium chloride, the minimum condenser spark

Table I.—Showing Results of Experiments upon the Explosion of the  $P_2O_5$ -dried  $2CO + O_2$  Mixtures.

No. of Expt.	Percentage Composition of the Gaseous Mixture.			Explosion Vessel Filled at :— T° C. & mm.	Drying Period Weeks.	Details of Firing Trials.	Final Pressure (corr.) of Cold Products mm.	Ratio $P_2/P_1$	Percentage Composition of the Gaseous Products.				Percentage CO Burnt.
	CO	O	N <sub>2</sub>						CO <sub>2</sub>	CO	O <sub>2</sub>	N <sub>2</sub>	
1	65.9	33.4	0.7	18.5° 744.2	25	(i) With 0.11 microfarads at 970 volta. $\Sigma = 0.052$ Joule. <i>No ignition.</i> (ii) With 0.50 microfarad at 970 volta. $\Sigma = 0.235$ Joule. <i>No ignition.</i> (iii) With 1.0 microfarad at 970 volta. $\Sigma = 0.47$ Joule. <i>Instant Explosion.</i>	544.0	0.73	66.7	19.8	11.8	1.7	77.2
2	65.6	33.4	1.0	17.0° 738.7	27	With 2.0 microfarads at 970 volta. $\Sigma = 0.94$ Joule. <i>Instant Explosion.</i>	527.0	0.715	81.5	11.1	5.5	1.9	88.0
3	65.8	33.5	0.7	16.5° 741.0	31	With 5.0 microfarads at 970 volta. $\Sigma = 2.35$ Joules. <i>Instant Explosion.</i>	526.0	0.71	80.8	11.7	5.9	1.6	87.5
4	66.2	33.0	0.8	19.0° 733.5	24	(i) With 0.5 microfarad at 970 volta. $\Sigma = 0.235$ Joule. <i>No ignition.</i> (ii) With 0.77 microfarad at 970 volta. $\Sigma = 0.362$ Joule. <i>Instant Explosion.</i>	551.5	0.75	64.0	22.2	11.8	2.0	74.3

discharge energy required for ignition seemed to be somewhere between 0.052 and 0.235 Joule (0.11 and 0.5 microfarad, respectively, at 970 volts). The resulting explosions were certainly sharper (a distinct "click" being usually audible) and the combustions more complete than was the case in the corresponding experiments with the  $P_2O_5$ -dried mixtures. Moreover, it was again observed generally that the greater the energy of the igniting spark the more complete the resulting combustion. Thus, in one experiment, when the energy of the igniting spark was 0.235 Joule (*i.e.*, 0.5 microfarad at 970 volts), combustion in the resulting explosion was only 91 per cent. complete; whilst in another, when it was 2.82 Joule (*i.e.*, 3 microfarads at 970 volts), the resulting combustion was 97.2 per cent. complete.

Such results suggest that, for a given degree of dryness of the mixture, the greater the ionising impulse imparted to it by the igniting spark, the more complete is the resulting combustion as the flame spreads through the explosive mixture; but this is a point which we wish to reserve for further investigation. Meanwhile, the experiments recorded in this paper undoubtedly prove:

- (1) That as water vapour is progressively removed from a  $2CO + O_2$  mixture, its "ignitibility" by condenser discharge sparks rapidly diminishes, the "minimum spark energy" necessary to fire it increasing until, with a calcium chloride-dried mixture, it becomes something like twenty or thirty-fold as great as that required to fire the same mixture when saturated with moisture at a temperature of  $15^\circ C$ .
- (2) That a  $2CO + O_2$  mixture which has been dried to an extreme degree by prolonged (six months) contact with pure phosphoric anhydride can still be ignited and exploded, provided that a spark of sufficient energy be passed through it, although the gases display a much greater "resistance" to combination than when even a minute amount of moisture is present.
- (3) That there is some property of the electric spark, presumably its ionising power, which, if only developed strongly enough, can overcome the high resistance of such an extremely dry mixture to ignition and explosion, and by virtue of which it can, so to speak, compensate the system for the absence of water vapour.

In conclusion, one of us (F.R.W.) desires to acknowledge his indebtedness to the Gas Light & Coke Company for his tenure of their Gas Research Fellowship at the Imperial College of Science and Technology, London, which has enabled him to devote his whole time to these and cognate researches.



*New Experiments upon the Combustion of Well-dried Carbon  
Monoxide and Oxygen Mixtures.—Part II.*

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[PLATE 3.]

(C) *Showing the Influence of Pressure upon the Ignitibility of a  $P_2O_5$ -dried  
 $2CO + O_2$  Mixture.*

For this third series of experiments a special form of apparatus (shown  
diagrammatically "in plan" in fig. 1) was set up, whereby the ignitibilities of  
 $2CO + O_2$  mixtures, whose components had been thoroughly dried (after

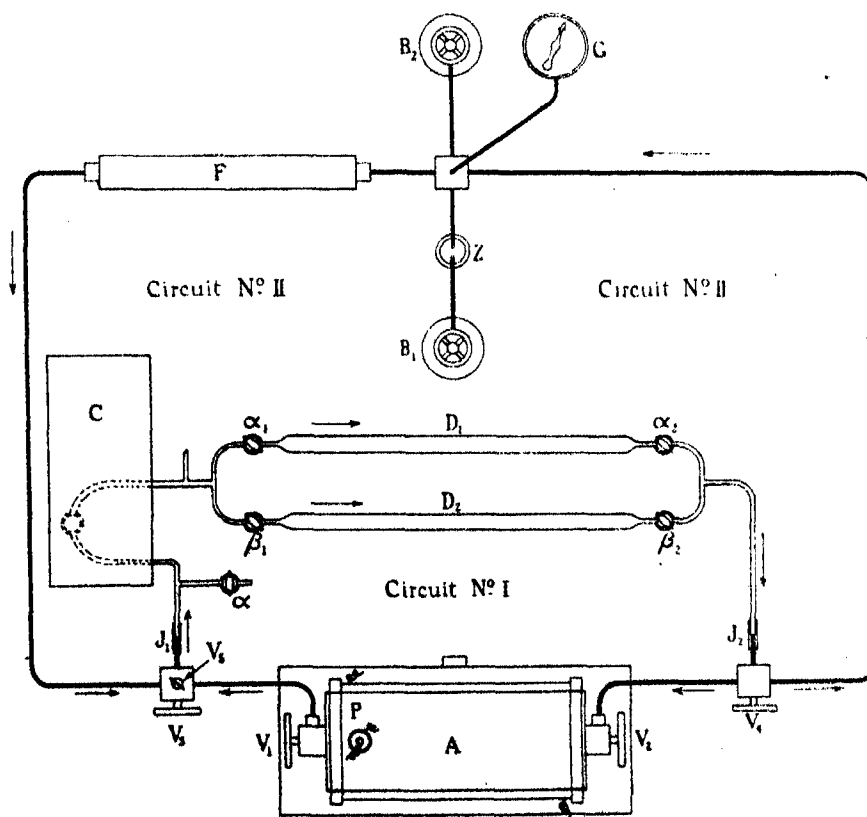


FIG. 1.

compression) over re-distilled phosphoric anhydride in small steel cylinders, could be tested in a nickel-steel bomb with a 1-in. diameter cylindrical explosion chamber at various initial pressures up to 20 atmospheres. The whole system and its connections had been previously thoroughly dried out by continuously circulating  $P_2O_5$ -dried nitrogen round it day and night for several months together. The following is a detailed description of the apparatus :—

#### *Apparatus.*

The nickel-steel cylindrical bomb A\* (with explosion chamber 8 inches long by 1 inch diameter, capacity 103 c.c.) was clamped horizontally to a special iron casting, which permitted of the bomb being rocked as and when required. This was bolted down to the experimental table, on to which were also fixed all the other items of the installation. The outside of the bomb, whose overall dimensions were 16 inches by 5 inches diameter, was wound with nichrome wire, so that it could be heated electrically to a temperature of  $150^{\circ}$  C. or more to facilitate the drying of it. It was fitted with a specially designed firing plug P, consisting of a central electrode (5 inches long by  $\frac{1}{8}$  inch diameter nickel-steel rod), which was wrapped round with an insulating packing of compressed mica to a thickness of  $\frac{5}{16}$  inch, in such a manner as to make a perfectly gastight joint even at high explosion pressures. It should be particularly noted that no organic substance whatever was employed in "packing" the firing piece, or indeed in any other part of the bomb or apparatus. The electrode of the firing piece projected about  $3\frac{1}{2}$  inches out of the body of the bomb in order to allow of a sufficiently high voltage being applied when a mixture had to be fired under high pressure. The bomb was closed at each end by the high-pressure steel valves  $V_1$  and  $V_2$ , respectively.

The carbon monoxide (previously prepared by dropping formic acid into warm pure sulphuric acid, and purified as described in Part I hereof) and the oxygen (98 per cent., prepared by fractionating liquid air, and subsequently passed through a strong solution of potassium hydroxide) were each separately introduced, under pressure, from large outside storage cylinders (where they had previously been compressed up to 120 and 170 atmospheres,† respectively) into one or other of the two small steel storage bottles  $B_1$  and  $B_2$  (capacity = 251 c.c.), where they were separately stored for at least a year, at pressures of

\* A detailed description of the bomb is to be found in 'Phil. Trans.,' A, vol. 215, pp. 280–1 (1915).

† The amount of water vapour in the thus compressed gases would certainly be less than 0.02 per cent. by volume, or lower than can be achieved by calcium-chloride drying.

60 and 90 atmospheres, respectively, in contact with 10 grams of pure redistilled phosphoric anhydride\* in each case.

The various parts of the apparatus were so arranged and connected up as to form two independent gas circuits round either of which, by suitably manipulating certain valves,  $P_2O_5$ -dried nitrogen could be continually circulated for weeks together for thoroughly drying out the whole system; of these—

*Circuit No. 1*—the drying circuit—was mainly constructed of glass and was used for the purpose of drying out the bomb and system by means of  $P_2O_5$ -dried nitrogen. It comprised (1) an automatic mercury circulating sprengel-pump, C, operated by means of re-distilled dry mercury with efficient external drying systems interposed between it and the outside atmosphere; (2) two glass drying tubes,  $D_1$  and  $D_2$  (each 18 inches long by  $\frac{3}{4}$ -inch diameter) filled with pure re-distilled phosphoric oxide, working in parallel, each drawn out at both ends and joined to a mercury sealed stopcock ( $\alpha_1 \alpha_2 \beta_1 \beta_2$ ); (3) the explosion bomb A, as indicated in the diagram. The glass portion of this circuit was connected with the bomb through two special glass-to-metal joints,  $J_1$  and  $J_2$  (details of which are shown in fig. 2) and the two pressure valves,

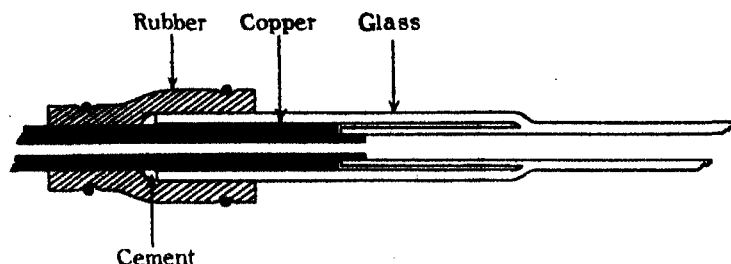


FIG. 5.

$V_3$  and  $V_4$  respectively, by closing which the glass section can be shut off from the pressure circuit. Communication with the outside could be made by opening the glass mercury sealed stopcock  $\alpha$  through which the apparatus could be exhausted by means of a Hyvac pump (not shown in diagram) and  $P_2O_5$ -dried nitrogen afterwards admitted.

*Circuit No. 2*—the “pressure system circuit” was entirely constructed of metal so as to be capable of withstanding a pressure of 200 atmospheres. It comprised (1) the bomb A; (2) high pressure valves,  $V_1$  to  $V_4$ , and a small pressure release valve  $V_5$ ; (3) a five-way brass connecting piece, through which connection was made with the two gas storage bottles,  $B_1$  and  $B_2$ ,

\* Previously prepared and tested as described in Part I hereof (q.v.).

each with its own control valve, and with the Bourdon pressure gauge, G, and (4) a glass-lined steel cylinder, F, 14 inches long by  $\frac{3}{4}$  inch internal diameter, containing 25 grams of pure re-distilled phosphoric anhydride.

Between the storage bottle, B<sub>1</sub>, containing the dried carbon monoxide at 70 atmospheres pressure and the five-way connection was inserted a small steel "trap," Z, which during the passage of the carbon monoxide from B<sub>1</sub> into the explosion bomb, A, was immersed in a vessel of liquid air for the purpose of freezing out any trace of iron carbonyl which might have been formed during the storage of the gases, a precaution which was considered necessary in the circumstances. Previous to connecting up the different parts of the installation, the inside of each of the two gas storage bottles, B<sub>1</sub> and B<sub>2</sub>, had been thoroughly cleaned out, so as to be quite free from rust or grease, after which they were kept for some time at 400° C. A similar procedure was also adopted both with the bomb itself and with all other metal parts and connections of the apparatus. The volume of the system comprising circuit No. 1 was 550 c.c. (including the bomb itself = 103 c.c.) whilst the volume of circuit No. 2, also with bomb, was 380 c.c.

#### *Experimental Procedure.*

Omitting unnecessary details as to the manipulation of the control valves and other incidental matters, the method of conducting the experiments may be described as follows. It comprised the following operations each separately performed :—

- (1) The drying out of the bomb.
- (2) The successive introduction of each of the two dried gases through the P<sub>2</sub>O<sub>5</sub>-drying tube, F, into the bomb, and then mixing therein in as near the desired proportions as could be conveniently managed.
- (3) The actual firing trials.

The compositions, both of the mixture fired and of the exploded gases, were always subsequently determined by analysis.

The bomb and its adjacent parts between V<sub>3</sub> and V<sub>4</sub> were thoroughly dried out by keeping the P<sub>2</sub>O<sub>5</sub>-dried nitrogen continually circulating day and night round Circuit No. 1 for not less than 20 weeks, the body of the bomb being kept at 150° C. during the last three, and the other metal parts frequently heated with a bunsen flame. During the first three-quarters of the drying the P<sub>2</sub>O<sub>5</sub>-tube, D<sub>1</sub>, only was put into circuit; afterwards it was cut out, and tube D<sub>2</sub> substituted for the final stages. In this way the use of fresh P<sub>2</sub>O<sub>5</sub> during the final stages was ensured, although only the first inch of the phosphoric anhydride

in  $D_1$  ever showed any sign of becoming moist, the rest of it as well as the whole of that in  $D_2$  remained perfectly dry and powdery throughout the whole of the period. By closing the valves  $V_1$  and  $V_2$  the  $P_2O_5$ -dried nitrogen is made to pass round circuit No. 2 in order to thoroughly dry out the rest of the system, an operation which likewise extended over several weeks continuously with similar heating out of all the metal connections at frequent intervals.

To give an idea of the time allowed for drying out the gases and the bomb system, etc., we may say (1) that the gases themselves had been in contact with the re-distilled phosphoric anhydride in the storage bottles  $B_1$  and  $B_2$  for (in one series) 52 weeks and (in another) for 20 weeks before being used in the experiments; and (2) that for the drying-out of the bomb and other connections in the manner already described, continuous periods of 22 and 65 weeks respectively were allowed. Thus there can be no doubt but that the drying both of the gases and of the bomb, etc., was pushed as far as phosphoric anhydride was capable of under the experimental conditions.

*Explosion of the Dried Mixtures.*—At the conclusion of the long drying operations the bomb and all its connections were cooled to room temperature and thoroughly evacuated through the stop-cock by means of a high-vacuum pump. Then, after closing the pressure valves  $V_3$ ,  $V_4$  and  $V_2$  sufficient of each of the  $P_2O_5$ -dried gases in succession was transferred very slowly under its own pressure from the storage bottles  $B_1$  and  $B_2$ , via the  $P_2O_5$ -drying tube  $F$  and valve  $V_1$ , into the bomb,  $A$ , where the explosive mixtures for the ignition trials were made. The volumetric ratio  $CO/O_2$  in these mixtures varied between 55/40 and 64/32 in different experiments. In the explosion chamber of the bomb was a smooth bronze sphere of  $\frac{3}{8}$ -inch diameter, the rolling of which to and fro a few times (by rocking the bomb on its carriage) ensured perfect mixing of the gases before the actual firing tests.

*Sparkling Arrangements.*—Two series of experiments were made, in each of which a spark gap of 1/100-inch was employed. In the first series the spark was obtained from a 1-inch Marconi induction coil, with a current of 6 volts in the primary circuit. In the second series, a motor-driven C.A.V. starting magneto, geared so as to give eight sparks per revolution of the drive, was used, together with a variable external gap (0 to 8 mm.).

*Experimental Results.*—The results of both series of experiments, the details of which are shown in Tables I and II (*q.v.*) showed:—

- (1) That, at pressures below two atmospheres, none of the mixtures could be ignited by the sparking devices used, no matter how many trials were made.

Table I.—Showing Results of First Series of Ignition Trials with Dry  $2\text{CO} + \text{O}_2$  Mixture under Pressure (1st Series).

Experi- ment No.	Time of Drying.		Initial Pres- sure.	Composition of Gases.								Per cent. Com- bus- tion.	Remarks.
	Bomb (weeks).	Gases (weeks).		Before Firing.			After Firing.						
				CO	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	CO	O <sub>2</sub>	N <sub>2</sub>			
1	22	53	1.0	63.6	33.1	3.2	—	—	—	—	Nil	Could not be fired.	
2	22	53	1.5	63.7	32.6	3.7	—	—	—	—	Nil	Could not be fired.	
3	22	53	3.0	59.0	36.8	4.2	67.6	7.4	21.7	3.4	90.1	Fired after sev- eral attempts.	
4	22	53	5.0	63.5	32.5	4.0	74.8	5.3	15.1	4.8	93.4	Fired at first attempt.	
5	22	53	10.7	60.2	32.0	7.7	88.6	0.8	1.5	9.1	99.1	Fired at first attempt.	
6	21	52	19.0	54.6	41.6	3.8	73.3	0.5	22.6	3.6	99.3	Fired at first attempt.	

Table II.—(2nd Series.)

Experiment No.	Time of Drying.*		Initial Pressure.	Composition of Gases.								Per cent. Combustion.	Remarks.
	Bomb (weeks).	Gases (weeks).		Before Firing.			After Firing.						
				CO	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	CO	O <sub>2</sub>	N <sub>2</sub>			
1	65	20	1.0	63.6	32.8	3.5	—	—	—	—	Nil	Did not fire after 100 sparks.	
2	65	20	2.0	60.5	35.6	3.9	—	—	—	—	Nil	Did not fire after 100 sparks.	
3	65	20	2.75	53.8	42.0	4.1	55.25	2.53	38.2	4.0	95.7	Fired after 100 sparks.	
4	65	20	5.2	58.1	37.6	4.2	67.3	7.0	20.6	4.9	91.7	Fired first spark.	
5	65	20	10.0	59.8	37.3	3.0	84.0	0.9	10.9	4.2	99.0	Fired first spark.	

\* In the interval between this and the previous series the gas storage bottles B<sub>1</sub> and B<sub>2</sub> were recharged at 70 atmospheres, the drying of the system being continuous throughout.

- (2) That, at initial pressures between 2.75 and 5.0 atmospheres, the mixture could be ignited (usually, however, only after several attempts), but that in the resulting explosion combustion was never quite complete, between 5 and 10 per cent. of the original carbon monoxide remaining unburnt.
- (3) That, at initial pressures of 10 atmospheres or more, the mixture always ignited instantaneously, at first shot, and that in the resulting explosion combustion was always 99 per cent. or more, complete.

It would thus appear that, although the "resistance to combustion" of such thoroughly  $P_2O_5$ -dried mixtures of carbon monoxide and oxygen was so great as to preclude their ignition at atmospheric pressure by means of the sparking arrangements employed in our experiments, yet on increasing the pressure they became ignitable, though at first not completely combustible, until at initial pressures of 10 atmospheres or more they were always easily ignited at first shot and readily exploded with complete combustion. Therefore, it may be concluded that, whilst the presence of water-vapour is undoubtedly helpful, it is not essential to the ignition and explosive combination of carbon monoxide and oxygen mixtures, but that, on the contrary, these gases can, and under high pressures readily do, combine directly.

(D) *Spectrographic Evidence. Spectrograms of CO-Air Flames burning under Pressure showing no "Steam Lines."*

The last section of the investigation deals with the evidence of the spectro-scope, which must be admitted as conclusive, so far as it goes. For, although we are only on the threshold of this part of the work, already several spectrograms have been obtained of explosion-flames of well-dried CO-air mixtures fired at initial pressures of 25 atmospheres and upwards, in which none of the characteristic ultra-violet "steam lines" emitted by burning hydrogen are discernible.

It will be remembered that in the two papers on "The Flame Spectra of Carbon Monoxide and Water Gas" recently published from these laboratories by Mr. F. R. Weston,\* conclusive proof was given that in a flame of pure (undried) carbon monoxide burning at atmospheric pressure in either air or oxygen two sets of independent interactions occur simultaneously—namely, (a) direct interactions between carbon monoxide and oxygen, exciting radiations which give rise to the continuous and banded parts of the spectrum, and (b) interactions between CO and  $OH_2$  molecules which originate the "steam lines"

\* 'Roy. Soc. Proc.,' A, vol. 109, pp. 176-86 and 523-6 (1925).

in the spectrum. And more particularly, it was shown that in the spectrogram of a flame of  $\text{H}_2\text{SO}_4$ -dried carbon monoxide, maintained in an atmosphere of  $\text{H}_2\text{SO}_4$ -dried oxygen, although the continuous and banded parts remained undiminished, the "steam lines" had become exceedingly faint.

During the past six months our new cylindrical bomb, with an explosion chamber 100 cms. long by 5 cms. internal diameter, fitted with quartz windows at each end, and otherwise specially designed for the spectrographic investigation of explosion flames under high pressures, has been successfully installed, and is now in full working order. And, although we wish to defer describing it in detail until a future paper, when more results will be available for discussion,\* we will now briefly explain our experimental procedure in obtaining photo-spectrograms of well-dried CO-air explosion flames under pressure. This will be understood from the accompanying diagram (fig. 3) in conjunction with the following brief description.

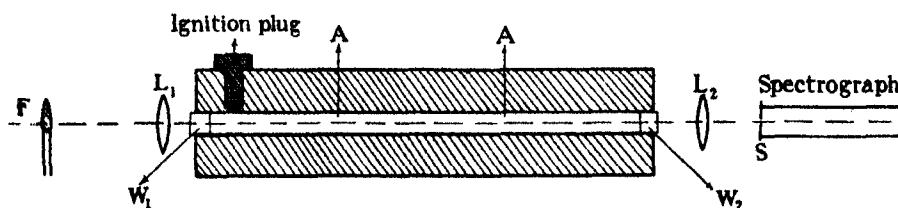


FIG. 3.

Immediately before the first experiment the cylindrical explosion chamber, A A, of our bomb had been thoroughly cleaned and dried out in a current of hot  $\text{P}_2\text{O}_5$ -dried nitrogen passed through it continuously for a fortnight, the body of the bomb being kept most of the time at above  $120^\circ\text{C}$ . by the external application of heat. At the end of this "drying period" the external source of heat was removed and the body of the bomb allowed to cool down to the room temperature. Whereupon  $\text{P}_2\text{O}_5$ -dried carbon monoxide and  $\text{P}_2\text{O}_5$ -dried air were successively introduced and mixed in the bomb, so as to produce therein a mixture corresponding to  $2\text{CO} + 1\frac{1}{2}\text{O}_2 + 4\frac{1}{2}\text{N}_2$  ready for explosion at an initial compression of 25 atmospheres. The slit, S, of the Hilger No. E2 quartz spectrograph was then placed in position outside one end of the explosion chamber, and everything adjusted in readiness to take a photo-spectrogram of the resulting explosion flame advancing in a direction towards it. But, before firing the explosive mixture, a flame, F, of undried carbon monoxide

\* It may, however, be stated that the quartz windows were so fitted into the bomb that the system withstood, and was perfectly gas-tight, at explosion pressures of 500 atmospheres.

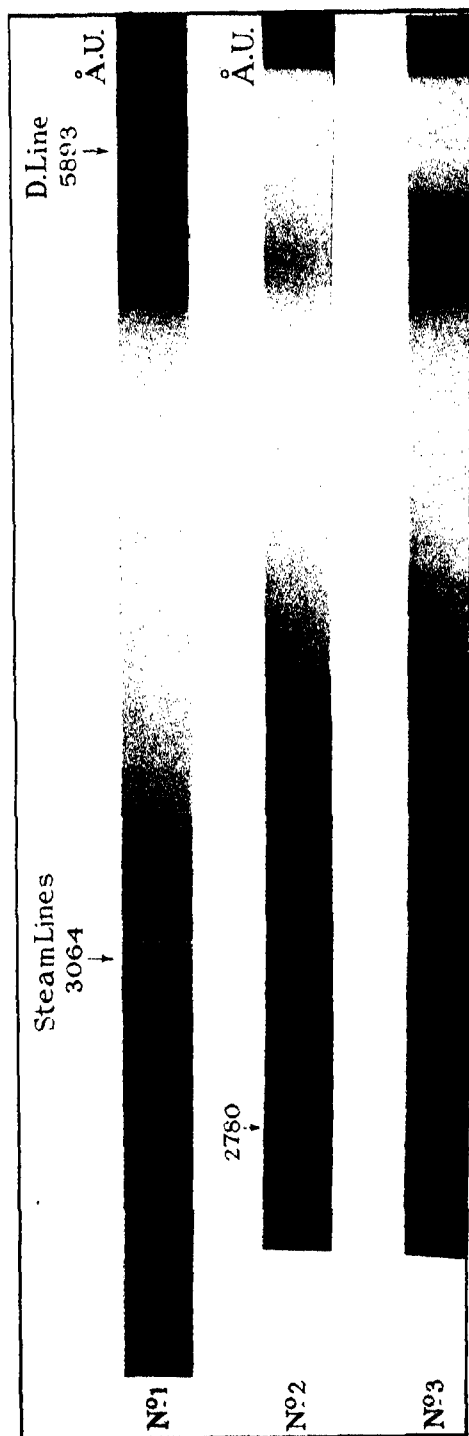


burning at a jet in air at atmospheric pressure was placed at the other end outside the bomb, in alignment both with the principal axis thereof and with the slit of the spectrograph; and by means of an arrangement of quartz lenses,  $L_1$  and  $L_2$ , a parallel beam of the radiation of the flame was sent right through the explosion chamber, A A (now containing the dry CO-air mixture under 25 atmospheres pressure) and its quartz windows,  $W_1$  and  $W_2$ , the emergent beam being afterwards focused on to the slit, S, of the spectrograph.

In this way a spectrogram was obtained of an undried CO-air flame burning at ordinary pressure, the radiation of which had traversed right through the explosion chamber, containing the dry CO-air mixture to be exploded, as well as its quartz windows. The amount of carbon monoxide burnt in this preliminary test was about the same as that subsequently exploded in the bomb itself. The resulting spectrogram, which is reproduced in No. 1 of the accompanying Plate 3, is the regular CO flame spectrum, the ultra-violet not being appreciably diminished in intensity by having traversed the compressed mixture in the bomb. It shows quite unmistakably the "steam lines," due to radiations excited by CO and  $\text{OH}_2$  interactions, as well as the continuous and diffused band-spectrum, due to radiations excited by direct CO and oxygen interactions; this continuous spectrum extended up to 2200 AU in the ultra-violet.

This "preliminary test" having been concluded, the outside CO-flame was extinguished, and the photographic plate in the camera of the spectrograph changed for a new one. The  $\text{P}_2\text{O}_5$ -dried CO-air mixture in the bomb was thereupon fired, at an initial pressure of 25 atmospheres, by an electrically-glowed platinum wire in the firing piece at the end remote from the spectrograph, so that the resulting explosion flame would travel down the cylindrical chamber *towards* the slit of the spectrograph. The mixture ignited instantly, and the duration of the explosion flame was sufficiently long to give a very good photo-spectrogram, which is reproduced in No. 2 of the accompanying Plate 3. It shows a continuous and diffused band-spectrum extending up to 2780 AU in the ultra-violet, without any "steam lines" being discernible. The experiment was repeated several times, always with the same result.

Other similar experiments were afterwards made in which the  $\text{P}_2\text{O}_5$ -dried CO-air mixture was ignited from the end of the bomb nearest to the slit of the spectrograph, so that the resulting flame travelled *away from* the latter. One of the spectrograms obtained under the latter conditions is reproduced in No. 3 of the Plate 3; it again shows no "steam lines" (either emission or absorption), and in all other respects it is identical with No. 2. In other



No. 1. Flame of undried CO burnt at ordinary pressures in air.

No. 2. Explosion flame of CO-Air ( $2\text{CO} + 1\frac{1}{2}\text{O}_2 + 4\frac{1}{2}\text{N}_2$ ) fixed at an initial pressure of 25 atmospheres — the flame travelling towards the slit.

No. 3. Explosion of flame as in No. 2, but travelling away from the slit.



words, the result was the same no matter whether the radiation from the CO-air explosion flame traversed either (a) the unexploded mixture in front of it, or (b) the hot exploded products behind it, before reaching the slit of the spectrograph.

Prof. A. Fowler, F.R.S., who has kindly examined the spectrograms for us, confirms the foregoing observations ; and, in addition, he remarks that while the pressure explosion flame shows the banded part of the spectrum less distinctly than does the CO-flame burning at ordinary pressure, the bands involved appear to be exactly the same in the two cases. This means that the direct CO-oxygen interactions were the same in both cases.

Another interesting feature brought out in both of the CO pressure explosion flame spectrograms (Nos. 2 and 3) is the marked shortening in the ultra-violet, as compared with the ordinary CO-flame spectrum (No. 1). It therefore appears that when a CO-air mixture is exploded under high initial pressures some of the characteristic ultra-violet radiation is absorbed during the explosion itself ; in this connection it may be mentioned that a further experiment, not reproduced here, showed that the cold explosion products under the same high pressure do not absorb any of the radiation from a CO-flame.

The spectrographic evidence thus seems to be conclusive against any theory which postulates that water vapour *necessarily* plays an intermediary *chemical* rôle, involving the decomposition and regeneration of steam, in the combustion of carbon monoxide. For, if every CO molecule necessarily has to interact chemically with steam during its combustion in the sense referred to, then, no matter how minute the quantity of steam present in any particular circumstances, the effect of its repeated interactions in the system would be integrated in the resulting spectrum, and the characteristic "steam lines" should appear in undiminished intensity. Indeed, it might be inferred that the only effect of progressively diminishing the steam content of the reactive gases down to minute proportions, by chemical or other drying processes, should be (if anything) to intensify the "steam lines" in the resulting spectrum, because there would be less chance of the characteristic steam radiation being absorbed before reaching the spectrograph.

#### *Concluding Remarks.*

In view of the long conflict of opinion which there has been hitherto amongst chemists respecting the rôle played by steam in the combustion of carbon monoxide, we wish to make it perfectly clear that, whilst the experiments

recorded in this and the preceding paper prove beyond reasonable doubt that the presence of steam is not essential to the ignition and explosion of carbon monoxide and oxygen mixtures, but that the two gases can and do combine directly without its intervention, the spectroscopic evidence recently obtained by Mr. F. R. Weston in these laboratories (*loc. cit.*) shows unmistakably that in a CO flame (undried) burning at a jet in air or oxygen (also undried) at ordinary pressure, CO and OH<sub>2</sub> molecules also interact, and that both the *direct* and *indirect* oxidations go on simultaneously and independently. Indeed, it could not be seriously contended that CO and OH<sub>2</sub> molecules are incapable of interacting at the high temperatures of flames.

An increasingly high pressure undoubtedly favours the *direct* oxidation, so that at high initial pressures it predominates almost to the exclusion of the *indirect*; on the other hand, the presence of hydrogen in the burning mixture undoubtedly favours the *indirect* oxidation, so that in a water-gas flame at ordinary pressure the indirect predominates to the practical exclusion of the direct oxidation.

Again, the spectroscopic evidence shows that it is the radiation excited by the direct CO-oxygen interactions in the flame which give rise to the continuous and banded parts of its spectrum, and which, in the explosion of CO-air mixtures, under pressure, activates the nitrogen. On the other hand, it is the radiations which are excited by the CO-OH<sub>2</sub> interactions which give rise to the "steam lines" in the spectrum, and there is much evidence showing that these do not activate nitrogen.

The results of the Bone-Haward experiments at initial pressures of 50 atmospheres (*loc. cit.*), supported as they have been by those more recently obtained at medium initial pressures by R. W. Fenning at the National Physical Laboratory,\* show that hydrogen is more potent than its equivalent of steam as a promoter of the combustion of carbon monoxide in CO-air mixtures, and suggested that its function may be to dissolve continuously the relatively inert CO molecules into a more "active" condition (*e.g.*, into O atoms), "activated-steam" being continuously formed and regenerated in the process.

Such, in short, is the new evidence from experiments in our laboratories respecting the combustion of carbon monoxide, which must be taken into account in revising our theories upon the subject.

We must, however, beware of allowing our conclusions to outrun the facts; for, although we may now set aside the idea that the presence of steam is essential to the combustion of carbon monoxide, much more remains to be learned

\* 'Phil. Trans.,' A, vol. 225, p. 331 (1928).

before we would be justified in putting forward any new theory as a proven one. It may be hoped, however, that the further spectroscopic work now in hand will materially assist us in the further solution of the problem. Meanwhile, many considerations incline us to think that the true explanation of the matter will ultimately be found in the ionisation of one (or both) of the combining gases as a necessary precedent to their combustion, and that steam, besides acting chemically when present in sufficient concentration, may also promote such ionisation, even when present in much smaller quantities, by virtue of its high specific inductive capacity: or, possibly, by condensing upon the free negative electrons, it may hinder their recombination with the positive CO-ions, and so maintain the "reactivity" of the system.

In conclusion we desire to express our best thanks to the Government Grant Committee of the Society and to the Department of Scientific and Industrial Research for grants out of which the cost of the expensive apparatus employed in the foregoing experiments has been defrayed. Also, two of us (R.P.F. and D.M.N.) have been indebted to the Department of Scientific and Industrial Research, and one of us (R.P.F.) to Radiation, Ltd., also, for personal grants which have enabled us to devote our whole time to the work.

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*Gaseous Combustion at High Pressures. Part VI.—The Explosion of Argon- and Helium-Diluted Knall-Gases.*

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*Introduction.*

In this paper are recorded the results of experiments made during the past year upon the explosion of argon- or helium-diluted hydrogen- and CO-knall-gases at various initial pressures between 10 and 150 atmospheres. Nearly all of these were made in our nickel-chrome-steel bomb No. 3 (spherical explosion chamber of 239 c.c. capacity), particulars of which were given in the previous paper of this series\* (*q.v.*), the only exception being four experiments, all at

\* 'Roy. Soc. Proc.,' A, vol. 108, pp. 393-418 (1925).

initial pressures below about 50 atmospheres, which were made in our nickel-steel bomb No. 2 (spherical explosion chamber of 242 c.c. capacity).\*

Although in the course of these researches up to the end of 1924 we had carried out several experiments with argon-diluted CO-knall-gas at various initial pressures, chiefly for comparison with the corresponding nitrogen-diluted knall-gas, we had never been able to make any systematic comparisons between argon and helium-diluted knall-gases, through lack of sufficient helium for experiments at high initial pressures. Some time ago, through the kindness of Sir William Pope, we got a small supply of it, which enabled us to make a few preliminary experiments at initial pressures up to 50 atmospheres; but it was not until early in 1925, when we were presented by the U.S. Bureau of Mines in Washington, through the kindness of Dr. S. C. Lind, their chief chemist, with a cylinder containing 60 cubic feet of helium at a pressure of 45 atmospheres for the purpose of our experiments, that we were able to carry out the main part of our programme.

The experiments which we have thus been enabled to make have comprised a complete systematic study of the explosion of such mixtures as (1)  $2\text{H}_2 + \text{O}_2 + 6\text{R}$ , (2)  $2\text{CO} + \text{O}_2 + 4\text{R}$ , and (3)  $2\text{CO} + \text{O}_2 + 6\text{R}$  (where R = either argon or helium), at various initial pressures between 10 and 150 atmospheres. The results have a twofold value, namely (1) in that they enable us to compare the influence of two monatomic diluents of widely different densities upon the rate of pressure-development in a gaseous explosion, and (2) from the point of view of furnishing new data for calculating the volumetric heat capacities of carbon dioxide and steam at temperatures exceeding  $2500^\circ\text{C}$ . One of us (D. M. N.) is engaged upon the last-named and hopes shortly to present the results of his calculations to the Society.

In the tabulated results of our experiments:—

$P_i$  obs. = the initial pressure, in atmospheres, at which the mixture was actually fired.

$P_i$  coord. = the said initial pressure "corrected" for any deviation of the mixture fired from Boyle's Law.

\* As pointed out in our last paper, in comparing the results obtained with a particular explosive mixture, when fired at one and the same pressure in each of the two bombs in question, it is necessary to remember that, whereas the times required to attain the maximum pressure ( $t_m$ ) should be identical, and the observed ratios of the maximum to the initial pressure ( $P_m/P_i$ ) nearly so, the rates of cooling after the attainment of  $P_m$  would naturally differ, owing to the much greater massiveness of the walls of bomb No. 3 than those of No. 2.

- $P_{m \text{ obs.}}$  = the maximum pressure, in atmospheres, actually attained in the explosion.
- $P_{m \text{ corr.}}$  = the said maximum pressure "corrected" for any cooling during the actual explosion period, whenever the experimental data enabled it to be calculated.
- $P_m/P_i \text{ corr.}$  = the ratio of the said "corrected" maximum pressure to the said "corrected" initial pressure.
- $t_m$  = the time, in seconds, taken for the attainment of  $P_m$ .

*Purity of the Gases used.*

The helium used in the experiments was of 98 per cent. purity throughout; this was constantly checked by density determinations, nitrogen being the only recognisable impurity. From the large low-pressure cylinder in which it arrived at our laboratories it was re-compressed into smaller cylinders up to 150 atmospheres before being used in our experiments, all of which were made with the original diluent after such re-compression.

The argon used was purchased in cylinders from the British Oxygen Company, and as received usually contained between 10 and 15 per cent. of nitrogen, but no other impurity. Before being used in the experiments, most of the nitrogen was removed chemically by passing the gas slowly through a combustion tube packed with a mixture of quick-lime and magnesium powder maintained at red-heat. After re-compressing the gas thus purified for the experiments, its nitrogen content was found to have been reduced to below 2 per cent., which was deemed to be sufficiently small for our purpose.

The other compressed gases used (carbon monoxide, hydrogen and oxygen) had been prepared by the best available method, and their purities were always checked by analyses. It may be assumed that adventitious nitrogen was the only impurity present in the various explosive mixtures, and that the amount of it never exceeded between 2 and 3 per cent. The exact composition of the mixtures exploded was always determined by analysis; and at least two repeat experiments were always made with each mixture at each particular initial pressure, so as to ensure accuracy of the results.

*Deviation of the Experimental Mixtures from Boyle's Law at the Various Initial Firing Pressures.*

The deviation of the various experimental mixtures used from Boyle's Law at the different initial pressures had to be determined first of all by actually making compressibility measurements in the bomb upon them. The following



were the factors, so ascertained, by which the observed initial pressure in each case had to be multiplied in order to get the "corrected"  $P_i$  :—

Mixture.	Observed $P_i$ in Atmospheres.					
	10	50	75	100	125	150
$2H_2 + O_2 + 6He$ ..	0.980	0.968	0.958	0.950	0.942	0.936
$2H_2 + O_2 + 6Ar$ ..	1.002	1.022	1.021	1.023	1.022	1.021
$2CO + O_2 + 4He$ ..	0.992	0.984	0.980	0.976	0.968	0.962
$2CO + O_2 + 6He$ ..	0.989	0.978	0.974	0.970	0.962	0.953
$2CO + O_2 + 4Ar$ ..	1.009	1.023	1.033	1.040	1.043	1.054
$2CO + O_2 + 6Ar$ ..	1.015	1.034	1.043	1.048	1.052	1.064

It will be observed that at all pressures the ascertained "correction" for the corresponding helium- and argon-diluted mixtures were always of opposite sign, namely, negative and positive, respectively. It is important to bear this clearly in mind in considering the experimental results; because it is the "corrected" rather than the "observed"  $P_m/P_i$  ratio which should always be compared if a right judgment is to be arrived at respecting the relative influence of the two diluents upon the explosion.

A.—*The Influence of Varying Initial Pressures between 60 and 130 Atmospheres upon the Explosion of  $2H_2 + O_2 + 6He$ ,  $2H_2 + O_2 + 6Ar$ , and  $2H_2 + O_2 + 6N_2$ .*

*Mixtures (Table I).*

We set out to investigate first of all the behaviour of helium- and argon-diluted  $2H_2 + O_2$  mixtures on explosion at high initial pressures because, considering the almost negligible dissociation of steam (less than 1 per cent.) at the maximum temperatures and pressures attained in our experiments, and the presumably constant specific heats at all temperatures of the two monatomic diluents, it was hoped to obtain valuable data for calculating the specific heat of steam at high temperatures and pressures. We soon found, however, that, unless the  $H_2$ -knall-gas was considerably diluted with the monatomic gas, the mixtures were very liable to detonate at high initial pressures, rendering the resulting pressure-time records not sufficiently reliable for our purpose.

Fortunately, however, the drawback referred to was found to disappear when the  $2H_2 + O_2$  mixture was diluted with twice its own volume of either of the monatomic diluents. Accordingly, it was decided to study the behaviour of mixtures corresponding to  $2H_2 + O_2 + 6He$  and  $2H_2 + O_2 + 6Ar$ , respectively, on explosion at observed initial pressures of 64.3, 96.4, and 128.6 atmospheres; and for purposes of comparison, the behaviour of a similarly

$N_2$ -diluted knall-gas mixture,  $2H_2 + O_2 + 6N_2$ , was also investigated at the two extreme initial pressures of the series. It should be understood that bomb No. 3 was used in all the experiments of the series, and that no detonation occurred in any of them.

The experimental results which are detailed in Table I showed very little difference in the behaviours of the helium- or argon-diluted knall-gas during the actual explosion period. The time taken to attain the maximum pressure

Table I.—Showing the Results of Experiments upon  $2H_2 + O_2 + 6R$  (where  $R = He, Ar$  or  $N_2$ ) Mixtures.

All in Bomb No. 3.

$P_{\text{obs. atm.}}$	64.3			96.4		128.6		
Experiment No. ....	84	85	86	87	88	89	90	91
Mixture — $2H_2 + O_2$ diluted with .....	6He	6Ar	6N <sub>2</sub>	6He	6Ar	6He	6Ar	6N <sub>2</sub>
$P_i$ corrd. atm. ....	62.4	65.5	64.3	91.8	98.6	121.2	132.0	126.9
$P_m$ { obs. atm. .... corrd. atm. ....	555 560	585 589	425 438	850 855	920 925	1180 1185	1290 1295	1000 1018
$t_m$ secs. ....	<0.005	0.005	0.02	<0.005	0.005	<0.005	0.005	0.015
Ratio $P_m/P_i$ { obs. .... corrd. ....	8.63 8.97	9.09 9.00	6.60 6.81	8.8 9.31	9.54 9.38	9.18 9.77	10.03 9.82	7.7 8.0
$P$ fall in 1 sec. after $P_m$ atm. ....	397	383	235	595	580	785	785	520
Percentage fall in ditto .....	72.2	66.6	55.2	70.9	63.0	66.5	60.8	52.0
Probable $T_m$ (approx.) C° .....	2630°	2640°	1920°	2740°	2810°	2900°	2970°	2300°

( $t_m$ ) was always slightly shorter with the helium-diluted than with the argon-diluted knall-gas; and the "corrected"  $P_m/P_i$  ratios were always slightly higher with the latter than with the former at corresponding initial pressures. Also, doubtless owing to the greater mobility of helium than argon molecules, the helium-diluted explosion products cooled down from  $P_m$  at a rather faster rate than did the argon-diluted products. We calculate that the maximum temperatures attained in the explosions, allowing for 1 per cent. steam-dissociation, would range probably between about 2630° and 2970° C., according to the initial firing-pressure, being consistently about 0.5 per cent. higher in the argon- than in the corresponding helium-diluted experiments.

In the two corresponding experiments made with the nitrogen-diluted knall-gas, the time taken for the attainment of maximum pressure was decidedly

lower than when either of the two monatomic diluents were used; also, as might be expected, the "corrected"  $P_m/P_i$  ratios were much lower, and the rates of cooling down from  $P_m$  much less rapid. The maximum explosion temperatures would range between about  $1920^\circ$  and  $2300^\circ$  C., according to the initial pressure.

In fig. 1, A to F, are reproduced the pressure-time records obtained in the two extreme experiments ( $P_i = 64.3$  and  $128.6$  atmospheres, respectively)

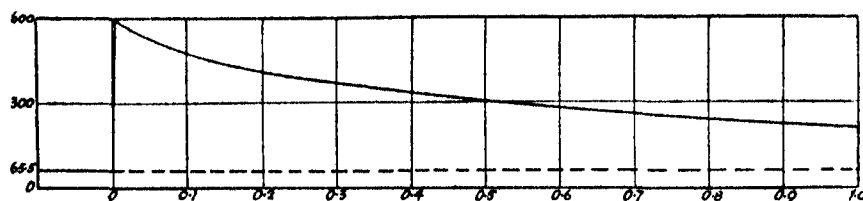


FIG. 1A.  $2H_2 + O_2 + 6Ar$ .  $P_i = 64.3$  Atmospheres.

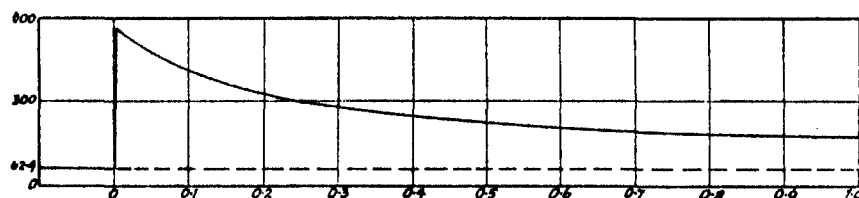


FIG. 1C.  $2H_2 + O_2 + 6He$ .  $P_i = 64.3$  Atmospheres.

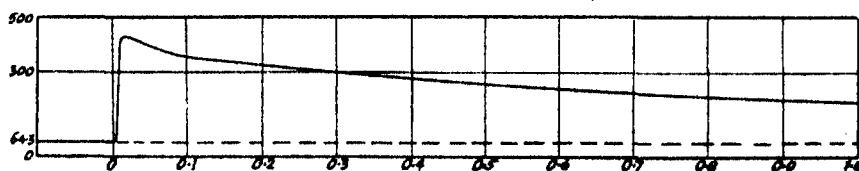


FIG. 1E.  $2H_2 + O_2 + 6N_2$ .  $P_i = 64.3$  Atmospheres.

Vertical scales represent Pressure in Atmospheres.

Horizontal scales represent Time in Seconds.

with each of the three mixtures. Some features of the  $P_m/P_i$  ratios, as well as the differentials of the cooling curves, will be further considered in the concluding section of the paper.

#### *B. The Behaviour of Helium- and Argon-Diluted CO-Knall-Gas Mixtures on Explosion at Various Initial Pressures.*

We next proceeded to investigate the behaviour on explosion, at different initial pressures up to 150 atmospheres, of helium- and argon-diluted CO-knall-gas mixtures of the compositions  $2CO + O_2 + 4R$  and  $2CO + O_2 + 6R$ ,

respectively. Here, however, undoubtedly the issues were complicated by the considerable degree of  $\text{CO}_2$ -dissociation at the maximum temperatures attained in the explosions, to which reference was made in the previous paper of this series\* (*q.v.*), and which rendered interpretation more difficult than otherwise it would be.

The results of the  $2\text{CO} + \text{O}_2 + 4\text{R}$  series of experiments, in which  $P_i$  was varied between 10 and 150 atmospheres, are detailed in Table II; those of

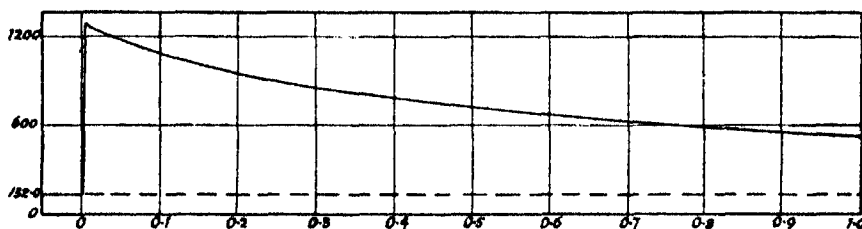


FIG. 1B.  $2\text{H}_2 + \text{O}_2 + 6\text{A}$ .  $P_i = 128.6$  Atmospheres.

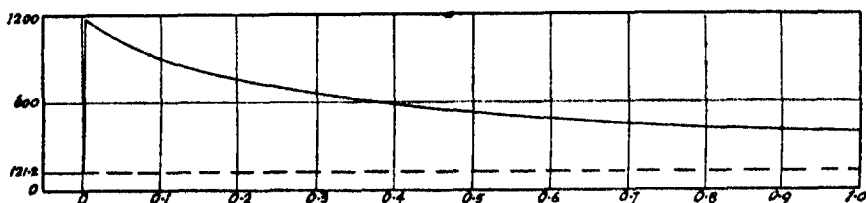


FIG. 1D.  $2\text{H}_2 + \text{O}_2 + 6\text{He}$ .  $P_i = 128.6$  Atmospheres.

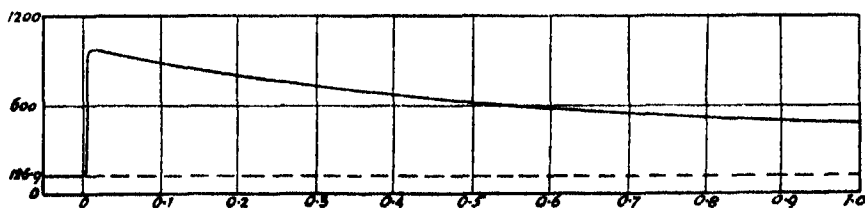


FIG. 1F.  $2\text{H}_2 + \text{O}_2 + 6\text{N}_2$ .  $P_i = 128.6$  Atmospheres.

Vertical scales represent Pressure in Atmospheres.

Horizontal scales represent Time in Seconds.

the  $2\text{CO} + \text{O}_2 + 6\text{R}$  series, where  $P_i$  was varied between 64.3 and 128.6 atmospheres, are shown in Table III. A selection of the pressure-time records are reproduced in figs. 2 and 3, from which their general character may be judged.

\* *Loc. cit.*, pp. 403-406.

Table III.—Showing the Results of Experiments with  $2\text{CO} + \text{O}_2 + 6\text{He}$  and  $2\text{CO} + \text{O}_2 + 6\text{Ar}$  Mixtures.

All in Bomb No. 3.

$P_i$ obs.	64.3		96.4		128.6	
Experiment No. ....	102	103	104	105	106	107
Mixture = $2\text{CO} + \text{O}_2$ diluted with ..	6He	6Ar	6He	6Ar	6He	6Ar
$P_i$ corrd. atms. ....	63.2	67.1	93.8	101.0	123.8	135.2
$P_w$ { obs. atms. ....	545	605	850	970	1170	1370
corrd. atms. ....	552	617	866	985	1190	1390
Ratio $P_w/P_i$ { obs. ....	8.5	9.0	8.81	10.1	9.10	10.65
corrd. ....	8.73	9.2	9.24	9.68	9.61	10.13
$t_m$ secs. ....	0.055	0.10	0.050	0.095	0.060	0.10
P fall in 1 sec. after $P_m$ atms. ....	230	225	330	325	436	445
Percentage fall in ditto ....	42.2	37.7	38.8	33.5	37.3	32.5

A close study of these results reveals certain persistent differences between the respective influences of the two monatomic diluents upon the explosion, to which attention may be directed. In the first place, the "corrected"  $P_w/P_i$  ratio was always materially (between 5 and 9 per cent.) higher in the argon-diluted than in the corresponding helium-diluted explosions. Now, although at first sight this might seem attributable to the lower density and greater mobility of helium molecules, as compared with those of argon, such an explanation is discounted by the fact that in the  $2\text{H}_2 + \text{O}_2 + 6\text{R}$  series of experiments, the  $P_w/P_i$  corrd. ratio for the helium-diluted knall-gas was never more than 1.0, and usually only about 0.5, per cent. higher than in the corresponding argon-diluted explosion (*vide* Table I). Therefore, we are driven to conclude that helium was influencing the explosion in some specific way other than as a monatomic diluent of low density. Here we must leave the matter for the moment, in the hope that a spectrographic investigation of it, which is now being undertaken, will help us in its further elucidation.

Another noteworthy circumstance was that, except in the case of the  $2\text{CO} + \text{O}_2 + 4\text{Ar}$  mixtures at initial pressures of 75 atmospheres or below, in none of the experiments did  $t_m$  vary much with the initial firing pressure. Curiously enough, however, whereas in the  $2\text{CO} + \text{O}_2 + 4\text{R}$  series at all initial pressures above 50 atmospheres, the helium-diluted were definitely slower than the corresponding argon-diluted explosions, the reverse was always the case

Table II.--Showing the Results of Experiments with  $2\text{CO} + \text{O}_2 + 4\text{He}$  and  $2\text{CO} + \text{O}_2 + 4\text{Ar}$  Mixtures.

$P_i$ obs.	Bomb No. 2.						Bomb No. 3.					
	10		50		75		100		125		150	
Experiment No.	92	38	93	21	94	95	96	97	98	99	100	101
Mixture = $2\text{CO} + \text{O}_2$ diluted with	4He	4Ar	4He	4Ar	4He	4Ar	4He	4Ar	4He	4Ar	4He	4Ar
$P_i$ corrd. atms.	9.7	10.1	49.4	51.15	73.7	77.5	97.6	104	121.1	130.2	144.3	158.1
$P_m$ { obs. atms.	84	89	470	510	710	790	940	1070	1200	1400	1490	1750
{ corrd. atms.	86	92	475	516	718	803	950	1080	1215	1415	1510	1768
$P_m$ secs.	0.025	0.050	0.025	0.025	0.025	0.015	0.025	0.010	0.02	0.010	0.02	0.010
Ratio $P_m/P_i$ { obs.	8.40	8.9	9.4	10.2	9.4	10.50	9.4	10.71	9.6	11.2	9.93	11.66
{ corrd.	8.65	9.1	9.6	10.1	9.7	10.35	9.75	10.4	10.0	10.9	10.4	11.20
$P$ fall in 1 sec. after $t_m$ atms.	60	44.0	216	204	345	335	415	443	492	540	590	660
Percentage fall in ditto	71.4	49.6	46.0	40.0	48.0	42.4	44.1	41.4	41.0	38.5	39.6	37.7

throughout the  $2\text{CO} + \text{O}_2 + 6\text{R}$  series. We think that the differences in question cannot have been due to mere "gauge-errors"; because, not only were they confirmed by duplicate experiments, but they were too consistent

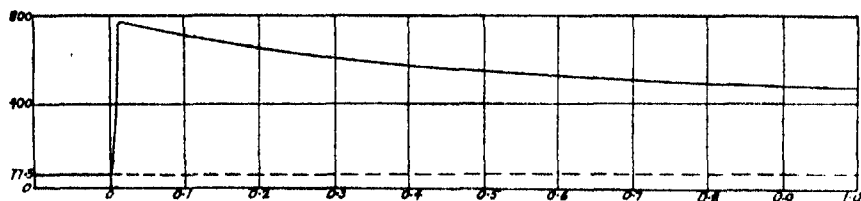


FIG. 2A.  $2\text{CO} + \text{O}_2 + 4\text{A}$ .  $P_i = 75$  Atmospheres.

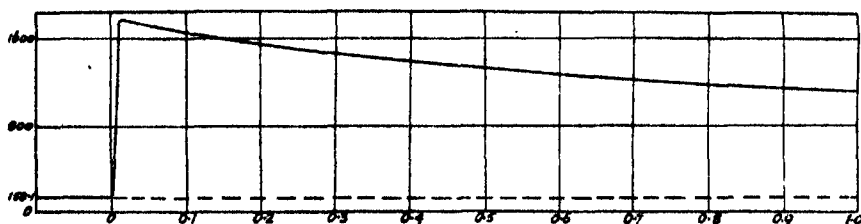


FIG. 2B.  $2\text{CO} + \text{O}_2 + 4\text{A}$ .  $P_i = 150$  Atmospheres.

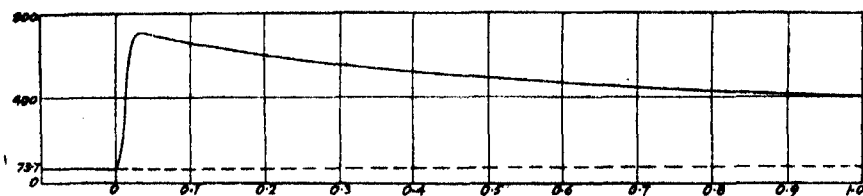


FIG. 2C.  $2\text{CO} + \text{O}_2 + 4\text{He}$ .  $P_i = 75$  Atmospheres.

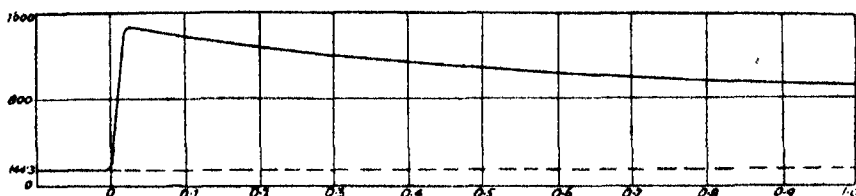


FIG. 2D.  $2\text{CO} + \text{O}_2 + 4\text{He}$ .  $P_i = 150$  Atmospheres.

Vertical scales represent Pressure in Atmospheres.  
Horizontal scales represent Time in Seconds.

to be so accounted for. Also, our Petavel gauge was working particularly well, and would almost certainly be sensitive to differences of 0.005 sec. (though not much less) in recording the  $t_m$ s.

It will be seen that, as might be expected, in corresponding experiments the rate of cooling from the  $P_m$  was always greater with the helium-diluted than with the argon-diluted explosion products. But, owing to the uncertainty of

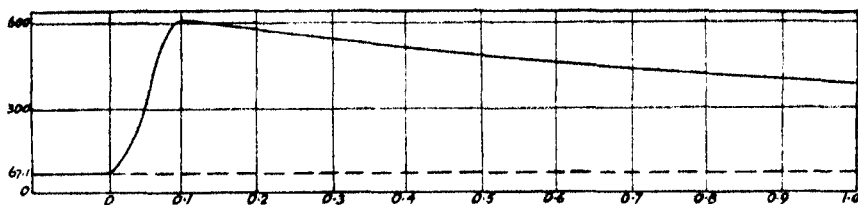


FIG. 3A.  $2\text{CO} + \text{O}_2 + 6\text{A}$ .  $P_i = 64.3$  Atmospheres.

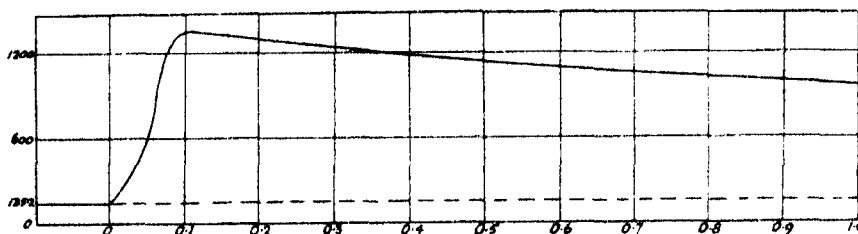


FIG. 3B.  $2\text{CO} + \text{O}_2 + 6\text{A}$ .  $P_i = 128.6$  Atmospheres.

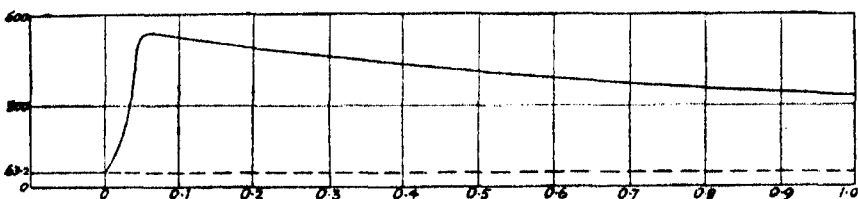


FIG. 3C.  $2\text{CO} + \text{O}_2 + 6\text{He}$ .  $P_i = 64.3$  Atmospheres.

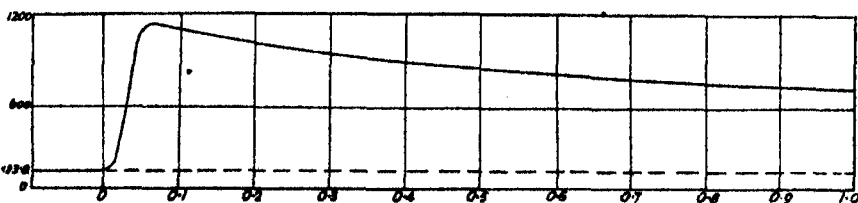


FIG. 3D.  $2\text{CO} + \text{O}_2 + 6\text{He}$ .  $P_i = 128.6$  Atmospheres.

Vertical scales represent Pressure in Atmospheres.

Horizontal scales represent Time in Seconds.

the degrees of  $\text{CO}_2$ -dissociation at the various maximum pressures attained in the explosions, it is not possible to give any reliable estimates for the corresponding maximum temperatures, and therefore we have not attempted to do so.



*C.—General Consideration of the  $P_m/P_i$  Ratios and the Cooling Curves.*

In the previous paper of this series\* we specially directed attention to the very remarkable way in which the "corrected"  $P_m/P_i$  ratios in explosions of diluted hydrogen- and CO-knall-gas mixtures always increase with the initial firing pressure; and we showed that such increases are independent either of deviations from Boyle's Law of the mixtures concerned under the experimental conditions, or of dissociation effects. We may now appropriately consider how the further results detailed in this paper have borne out what was then said.

Turning, first of all, to the  $2H_2 + O_2 + 6R$  and  $2CO + O_2 + 6R$  results, where R was a monatomic gas, we find as follows:—

Mixture.	$P_m/P_i$ corrected.		Percentage Increase.
	$P_i = 64.3$	$P_i = 128.6$	
$2H_2 + O_2 + 6He$ ....	8.96	9.77	9.0
$2H_2 + O_2 + 6Ar$ ....	9.00	9.82	9.0
$2CO + O_2 + 6He$ ....	8.73	9.61	10.1
$2CO + O_2 + 6Ar$ ....	9.2	10.13	10.1

Again, in the  $2CO + O_2 + 4R$  series, we find the following percentage increases in the "corrected"  $P_m/P_i$  values over the given  $P_i$  ranges:—

Mixture.	$P_i$ abs. Ranges.			Percentage increase in $P_m/P_i$ corr'd.
	10 to 75 atms.	75 to 150 atms.	10 to 150 atms.	
$2CO + O_2 + 4He$ ..	12.2	7.2	20.2	}
$2CO + O_2 + 4Ar$ ....	13.7	8.2	23.1	

There can be no doubt either as to the magnitude of the increase, or to its independence of any "dissociation" effects, because, for the range  $P_i = 64.3$  to 128.6, it was nearly as great in the case of the  $2H_2 + O_2 + 6R$  mixtures, where presumably such effects would be negligible, as it was in the case of the  $2CO + O_2 + 6R$  mixtures, where they would not be. The remarkable constancy of the increase, and the fact that it is always much greater over the  $P_i$  range 10 to 75 than over the range 75 to 150 atmospheres, suggests its connection with some fundamental physical feature of the explosion. In our

\* *Loc. cit.*, pp. 410–415.

last paper we suggested that it might be due to an increasing opacity of the gaseous medium with pressure to the radiation emitted during the explosion; and, so far as we have gone with them, our recent spectrographic experiments support this view of the matter.

In a private communication to us, Prof. W. T. David has made another suggestion, namely, that the specific heats of gases like carbon dioxide and steam,

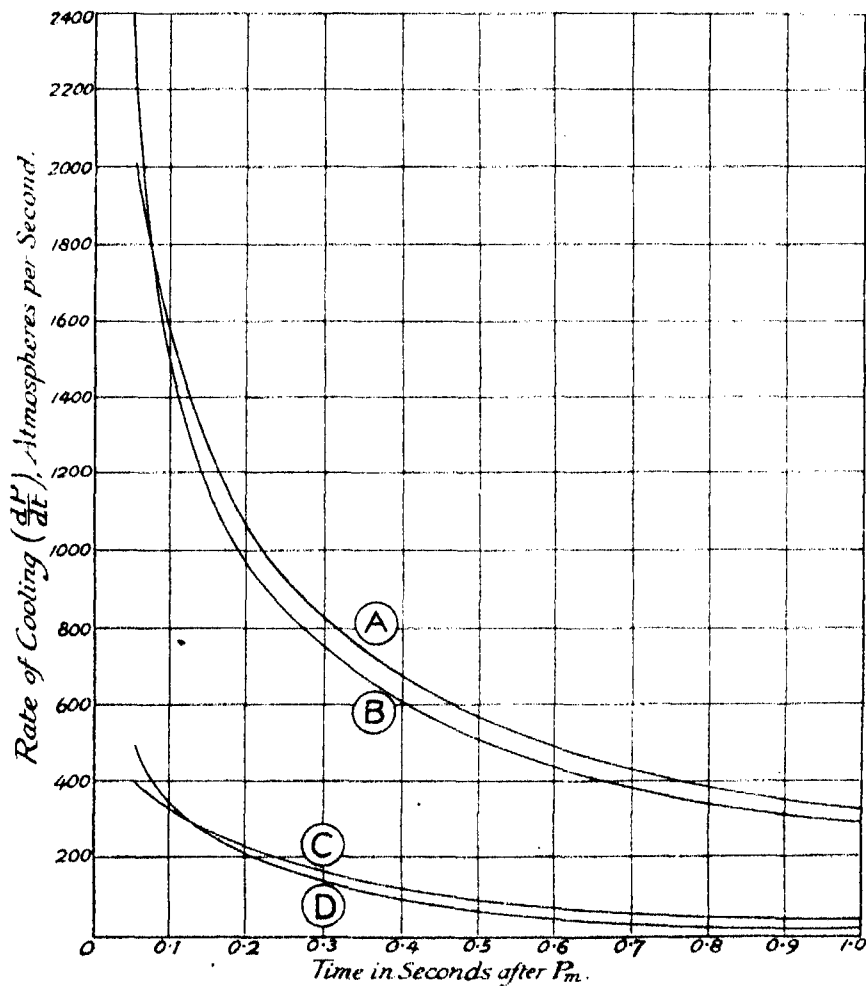


FIG. 4. "Differential" Cooling Curves.

Curve A.	$2\text{H}_2 + \text{O}_2 + 6\text{Ar}$	} $P_i = 128.6$ Atmospheres.
" B.	$2\text{H}_2 + \text{O}_2 + 6\text{He}$	
" C.	$2\text{H}_2 + \text{O}_2 + 6\text{Ar}$	} $P_i = 64.3$ Atmospheres.
" D.	$2\text{H}_2 + \text{O}_2 + 6\text{He}$	

which emit radiation when heated, decrease considerably as the density increases at temperatures at which they emit radiation strongly, and he is

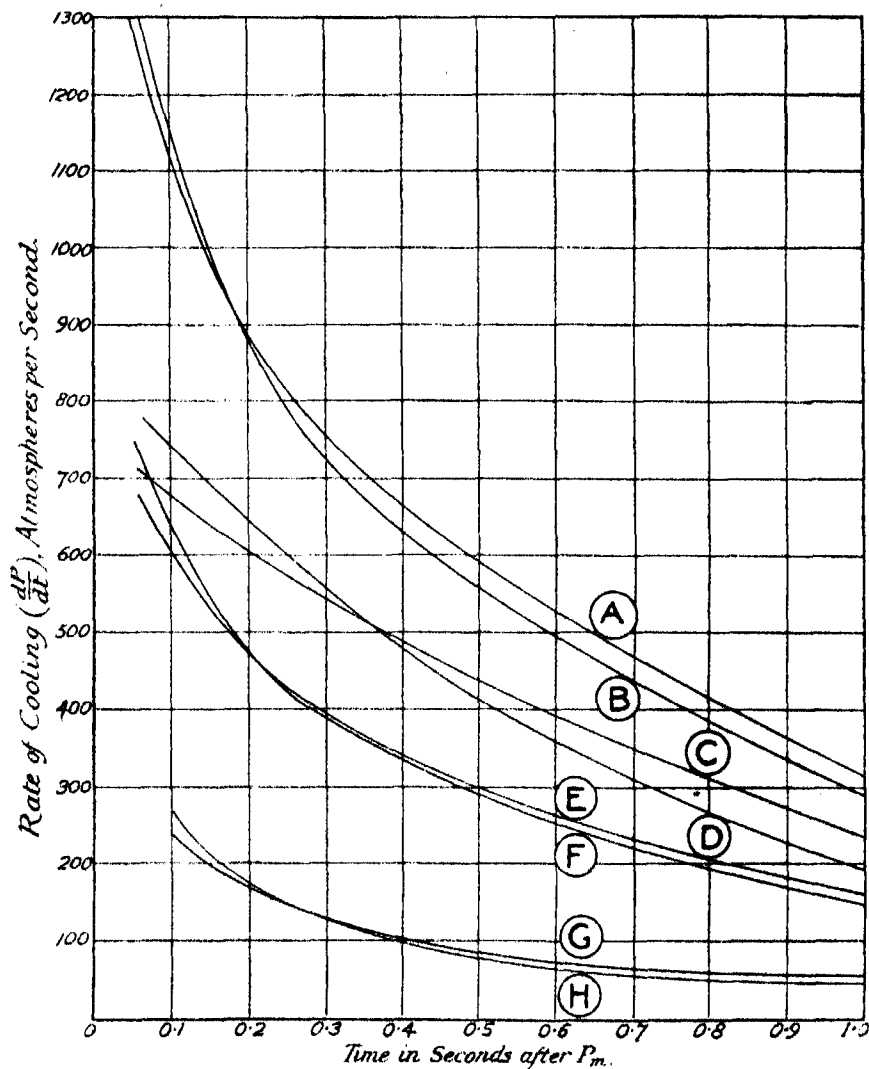


FIG. 5. "Differential" Cooling Curves.

Curve A.	$2\text{CO} + \text{O}_2 + 4\text{Ar}$	} $P_i = 150$ Atmospheres.
" B.	$2\text{CO} + \text{O}_2 + 4\text{He}$	
" C.	$2\text{CO} + \text{O}_2 + 4\text{Ar}$	} $P_i = 128.6$ Atmospheres.
" D.	$2\text{CO} + \text{O}_2 + 4\text{He}$	
" E.	$2\text{CO} + \text{O}_2 + 4\text{Ar}$	} $P_i = 75$ Atmospheres.
" F.	$2\text{CO} + \text{O}_2 + 4\text{He}$	
" G.	$2\text{CO} + \text{O}_2 + 4\text{Ar}$	} $P_i = 64.3$ Atmospheres.
" H.	$2\text{CO} + \text{O}_2 + 4\text{He}$	

publishing a detailed statement of his views upon the matter. Until further experiments have been made, however, we are unable to say more than that his suggestion is receiving careful consideration, and that we hope to be in a position to deal with it in some future paper.

In figs. 4 and 5 are reproduced the "differential" cooling curves, in which rates of cooling  $dP/dt$  in atmospheres per second are plotted against the time in seconds after the attainment of maximum pressure, for the  $2H_2 + O_2 + 6R$  and the  $2CO + O_2 + 4R$  (where  $R = He$  or  $Ar$ ) explosions at the two extreme initial pressures in each case. In all these explosions the time taken for the attainment of maximum pressure was so short (varying between 0.005 and 0.020 sec.), that the peak point of the "pressure-time curve" was very sharp, and the cooling immediately after  $P_m$  very rapid. An analysis of these curves shows that "radiation" factors played a considerable part in the cooling during the first 0.5 sec. after  $P_m$ , especially in the carbon monoxide explosions.

In conclusion, we thank both the Government Grant Committee of the Royal Society and the Department of Scientific and Industrial Research for continued grants in support of the work, which have not only met the cost of the bomb apparatus, but also have enabled one of us (D. M. N.) to devote his whole time to the research. Also, another of us (D. T. A. T.) returns thanks to the International Education Board for a Research Fellowship which has similarly enabled him to do the same. And, lastly, we desire to express our gratitude to Dr. S. C. Lind and the U.S. Bureau of Mines for their generous gift of the helium used in the experiments.

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*Measurements of the Amount of Ozone in the Earth's Atmosphere  
and its Relation to other Geophysical Conditions.*

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Oxford, and D. N. HARRISON, D.Phil.

(Communicated by Prof. F. A. Lindemann, F.R.S.—Received January 4, 1926.)

[PLATE 4.]

TABLE OF SYMBOLS.

The following symbols are used throughout this paper :—

- $\lambda$  = wave length.
- $\text{\AA}$  = Angstrom unit =  $10^{-8}$  cm.
- \* $k$  = absorption coefficient of atmosphere.
- $\delta$  = absorption coefficient due to particles large compared with  $\lambda$ .
- \* $\beta$  = absorption coefficient due to particles small compared with  $\lambda$ .
- \* $\alpha$  = absorption coefficient of 1 cm. of pure ozone at N.T.P.
- $x$  = thickness of equivalent layer of ozone.
- \* $I_0$  = intensity of radiation outside the earth's atmosphere.
- \* $I$  = intensity of radiation at surface of earth.
- \* $K$  = wedge constant.
- $y$  = ordinate (in measurement of photographs taken through a wedge).
- $z$  = sun's zenith distance.

§ 1. INTRODUCTION.

Several attempts have been made to determine the amount of ozone in the earth's atmosphere during recent years. Until 1920 only chemical methods were employed, and these yielded very discordant results, the difficulty being to separate the chemical action of ozone from that of other oxidizing constituents of the atmosphere.† Rayleigh‡ in England, and Götz§ in the Alps, have shown that there cannot be more than a very small amount of ozone in the air near the earth's surface. The first accurate measurements of the total amount of ozone in the atmosphere over any given region were made by Fabry and Buisson,|| who measured spectroscopically the intensity of the ultra-violet absorption band in the solar spectrum, which is due to ozone in the earth's atmosphere. From measurements made on 14 days in May and June, 1920,

\* Function of  $\lambda$ .

† Pring, 'Roy. Soc. Proc.,' vol. 90 (1914).

‡ Strutt, 'Roy. Soc. Proc.,' vol. 94 (1917-18).

§ Götz, 'Die Sterne'—Potsdam, August-September, 1925.

|| Fabry and Buisson, 'Astrophys. Journ.,' December, 1921.

they found the amount of ozone to be equivalent to a layer of pure ozone about 3 mm. thick at normal temperature and pressure. Small variations were observed from day to day.

Ozone has a very strong absorption band, extending from about  $3300 \text{ \AA}$  towards the shorter wave-lengths and reaching a maximum at about  $2550 \text{ \AA}$ , and a weak band in the visible, which, however, absorbs some 4 per cent. of the solar energy at  $6000 \text{ \AA}$ , and only rather narrow bands in the infra-red at about  $9.5\mu$  and  $4.5\mu$  (whose width and intensity are not accurately known); therefore its equilibrium temperature under solar and terrestrial radiation is high. It is thus of considerable interest to determine what variations in the amount of ozone take place over a long period, since these may have important relations to other geophysical phenomena.

Details of a scheme of measuring the amount of ozone daily, by a method similar in principle to that used by Fabry and Buisson, were worked out in 1924, and during 1925 observations were made on every day possible. The results have shown that there is a marked relation between the amount of ozone and the conditions in the upper atmosphere, and while the full details of this cannot be obtained from one year's observations, it seems worth while at this stage to place on record the values so far obtained, and the details of the method employed.\*

## § 2. THEORY OF MEASUREMENT OF THE ABSORPTION COEFFICIENTS OF THE ATMOSPHERE FOR ULTRA-VIOLET RADIATION, AND DEDUCTION OF THE AMOUNT OF OZONE.

Ozone has absorption bands between about  $3300 \text{ \AA}$  and  $2000 \text{ \AA}$ . The absorption of solar radiation is almost complete at  $2900 \text{ \AA}$ , and forms the limit of the solar spectrum at the earth's surface.

\*The amount of ozone in the atmosphere is obtained by taking spectrograms of sunlight, and measuring the intensity of the ultra-violet absorption band due to ozone. Since the absorption of sunlight is practically complete near the centre of the band, measurements can only be made near its long wave-length limit.

Two separate methods are possible: (a) (Long Method or Series.) We may obtain the actual atmospheric absorption coefficients for a number of wave-lengths by making observations at various altitudes of the sun, and so deduce

\* For brief summary of early results, see 'Quart. Journ. Roy. Meteor. Soc.,' October, 1925.

the amount of ozone. (b) (Short Method.) Having once obtained the necessary constants, we may assume the ratio of the intensities of light of two adjacent wave-lengths, as emitted by the sun, to remain constant. If these wave-lengths are chosen near the edge of the band, so that ozone absorption coefficients are very different, measurement of the relative intensities reaching the earth's surface may be used to give the amount of ozone.

While the second method involves assumptions about the sun, it only requires one photograph instead of a series, and in such a cloudy climate as that of England is the only one that can be used to give daily routine values.

§ 2 (a) *Long Method*.—Let  $I_0$  be the intensity of radiation of wave-length  $\lambda$  outside the earth's atmosphere, and  $I$  the intensity measured at the surface of the earth.

If the radiation were to pass normally through a layer of air of unit thickness, the intensity would be reduced to  $I_0 \times 10^{-a}$ , where  $a$  is called the coefficient of absorption of the air, and is a function only of the composition and density of the air.

After passing through a thickness  $x$ , the intensity would be

$$I_0 \times 10^{-ax}.$$

The air, however, is not constant in composition or density, but the former changes considerably, and the latter decreases, with height. Let  $a$  be the coefficient of absorption at a height  $h$  above the earth's surface. We assume here that the earth is flat, and that the air is uniform over any plane parallel to the surface, so that  $a$  is a function only of  $h$ . The error introduced by the curvature of the earth, and that due to refraction by the air, are quite negligible for values of  $\sec z$  less than 4 ( $z$  being the sun's zenith distance).

After passing through a thickness  $dh$  at an angle  $z$  to the normal,  $I_0$  is reduced to

$$I_0 \times 10^{-a \sec z \, dh},$$

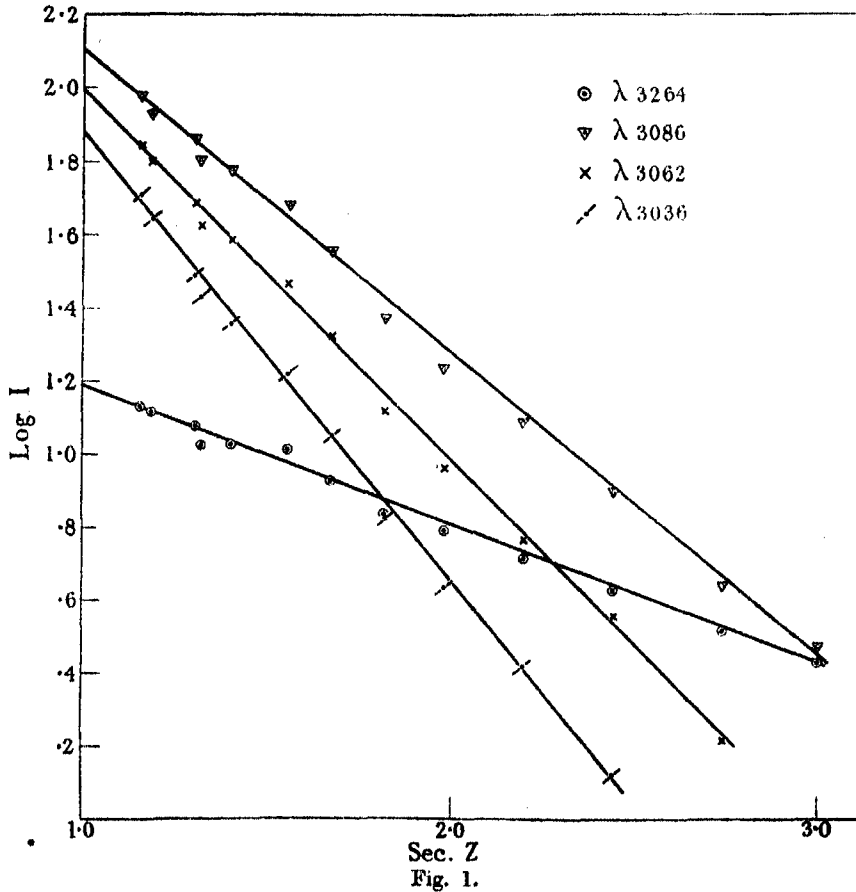
since the thickness of the layer is effectively  $x = dh \cdot \sec z$ .

Thus

$$\begin{aligned} \text{Log } I &= \text{log } I_0 - \int_0^{\infty} a \sec z \, dh \\ &= \text{log } I_0 - k \sec z, \end{aligned} \tag{i}$$

where  $k = \int_0^{\infty} a \, dh$ .  $k$  is, therefore, independent of  $z$ , and is called the coefficient of absorption of the atmosphere (for vertical transmission).

The intensity of the solar radiation which reaches the earth's surface is measured in arbitrary units for about 10 wave-lengths between 3300 and 2900 Å, at different times during the same morning or afternoon. (This is described in § 2 (b).) The logarithms of these values to the base 10 are plotted against  $\sec z$  (fig. 1).



Equation (1) shows that  $\log I$  is a linear function of  $\sec z$ , provided that  $I_0$  and  $k$  remain constant during a series of observations. It is not likely that  $I_0$  varies appreciably during one day, and any irregular changes of  $k$  will appear when the points are plotted.\* These points (fig. 1) should lie on a straight line, the tangent of whose inclination to the  $\sec z$  axis is equal to  $k$ . Hence  $k$  is found for any desired number of wave-lengths.

\* See § 5 (a) (i).



The loss of light due to scattering in the atmosphere can be roughly divided into two classes—that which is due to particles small compared with  $\lambda$ , and is proportional to  $\lambda^{-4}$ , and that which is due to large particles (so-called dust, including water drops), and is independent of  $\lambda$ .\*

Fabry and Buisson assumed that the only small particles were air molecules, and used calculated values for the absorption coefficient due to scattering of this class. But it is certain that there are other small particles which scatter according to the  $\lambda^{-4}$  law, or possibly some other law. This method measures the actual values of the absorption coefficients of the atmosphere, and assumes nothing about the particles to which they are due.

If  $k$  is plotted against  $\lambda^{-4}$ , the curve should be a straight line for wave-lengths greater than about 3300 Å (the beginning of the ozone absorption); after this, however,  $k$  increases very rapidly, owing to the ozone absorption (fig. 2).

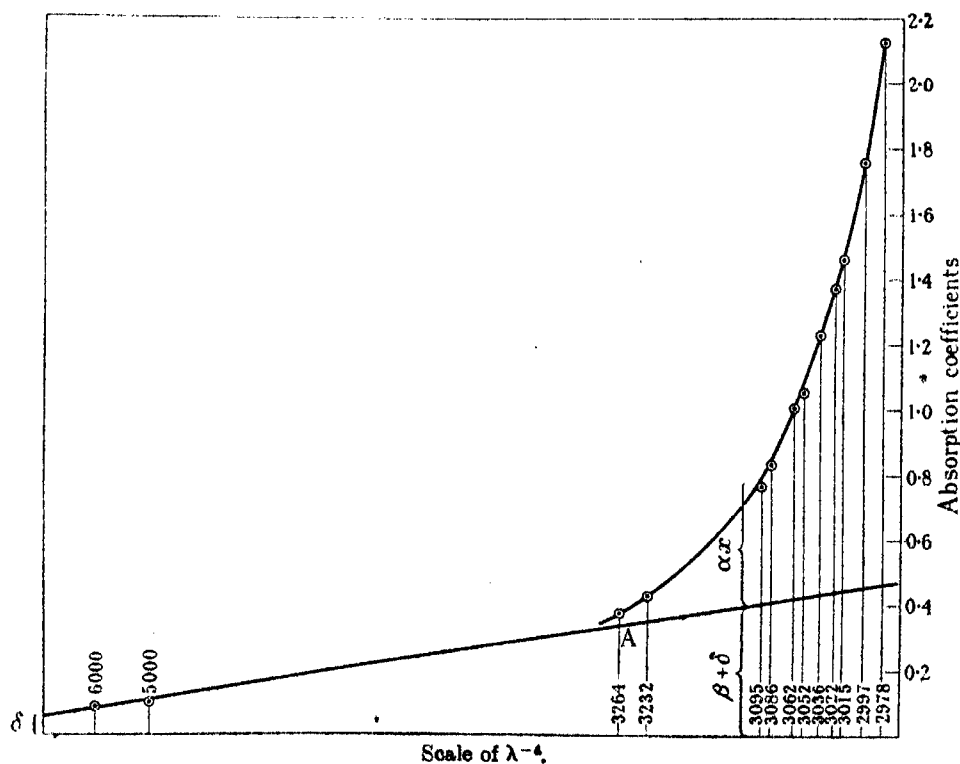


Fig. 2.

\* In justification of this see 'Smithsonian Misc. Collections,' vol. 69, No. 2.

Let  $\beta$  be the absorption coefficient due to scattering by small particles for  $\sec z = 1$ .

$\delta$ , the same for large particles.

$\alpha$ , the absorption coefficient for 1 cm. thickness of pure ozone at N.T.P.,  
and

$x$ , the thickness in cms. which the ozone actually present would have  
if reduced to a uniform layer at N.T.P.,

assuming that the absorption does not vary with temperature or pressure.

Then  $I_0$  is reduced in the ratio  $10^{-\beta \sec z}$  by scattering by small particles, in the ratio  $10^{-\delta \sec z}$  by large particles, and in the ratio  $10^{-\alpha x \sec z}$  by absorption by ozone. Therefore, we suppose that

$$I = I_0 \times 10^{-\beta \sec z} \times 10^{-\delta \sec z} \times 10^{-\alpha x \sec z}$$

and

$$k = \beta + \delta + \alpha x, \quad (2)$$

since no other constituent of the atmosphere is known to absorb in the region of the spectrum with which we are dealing.

For wave-lengths greater than 3300 Å,  $\alpha = 0$  and  $k = \beta + \delta$ , so that  $k$  is a linear function of  $\lambda^{-4}$ ; and by extrapolating the straight part of the curve to wave-lengths less than 3300 Å, we can obtain the value of  $\beta + \delta$  for any wave-length.

That part of the ordinate, for any wave-length, which lies above the extrapolated curve, is equal to  $k - (\beta + \delta)$ , or  $\alpha x$ .

We thus find  $\alpha x$  for several wave-lengths in the region of ozone absorption, viz., from about 3100 Å to the limit of the solar spectrum.

The following values of  $\alpha$  are calculated from the empirical formula given by Fabry and Buisson.\*

Table I.

$\lambda$ ...	3264	3232	3095	3086	3062	3052	2036	3022	3015	2997	2978
$\alpha$ ...	0.15	0.22	1.35	1.50	2.05	2.33	2.88	3.44	3.75	4.75	6.03

Dividing  $\alpha x$  by  $\alpha$  gives the value of  $x$ , the thickness of the equivalent layer of ozone at N.T.P. The values of  $x$  obtained ought, of course, to be the same for all wave-lengths.

In the next section will be described the method of making the measurements of intensity which give the points in fig. 1, and details in the construction of fig. 2.

\* Fabry and Buisson, 'Journ. de Phys.,' (5) 3, 196 (1913).

§ 2 (b). Photographs of the sun's spectrum in the region 3350 to 2900 Å are taken with a quartz spectrograph. The radiation, before falling on the plate, passes through an optical wedge placed against the plate, with its lines of equal density parallel to the dispersion.

If  $i$  is the intensity (uniform over the whole height of the image) of any wave-length  $\lambda$  incident on the wedge, the intensity, at any point, of the radiation which falls on the plate is

$$i \times 10^{-Ky}, \quad (3)$$

where  $y$  is the distance of the point from the line of zero density of the wedge, and  $K$  is called the wedge constant for wave-length  $\lambda$ . A line  $\lambda$ , therefore, as it appears on the plate, decreases in density from one end to the other.

Six spectra, at six different values of  $\sec z$ , are taken on the same plate, with equal times of exposure (30 secs.). About 12 photographs altogether are taken on one morning or afternoon. (These will be referred to as a "series.") In order to make all plates comparable, by eliminating variations in development and sensitivity, a strip of the plate is exposed to a uniform, constant light for 30 secs. This exposure is the same for all plates.\* The source of light is a 12-volt gas-filled lamp, run at 9 volts.† The light from the lamp passes through a piece of Chance's ultra-violet glass, which transmits a trace of the extreme red and a band in the ultra-violet with a maximum at about 3600 Å.

The plate is measured with a photometer at certain fixed wave-lengths, and the distances, from the thin end of the wedge (or rather from a reference line near this end) to the points where the density is equal to the density of the standard strip, are recorded. The wave-lengths chosen are well-marked Fraunhofer transmission spaces. The distances so measured we call  $y$ .

Then, since the density of the standard strip corresponds to a constant and invariable intensity (though of a different wave-length from any of these in the spectra), we have, from equation (3)

$$i \times 10^{-Ky} = \text{constant}.$$

Thus  $y$  is a measure of  $i$ , the intensity of wave-length  $\lambda$ , and we have the equation

$$\log I = Ky. \quad (4)$$

\* For description of the optical wedge and of the method of standardizing the plates, see 'Photographic Photometry,' by G. M. B. Dobson, I. O. Griffith and D. N. Harrison (Clarendon Press).

† For a discussion of constant sources of light, see "Photoelectric Photometry," G. E. C. Research Staff—'Journ. Sci. Inst.,' October, 1925.

The ordinates plotted in the  $\log I - \sec z$  curves (fig. 1) are therefore the values of  $K_y$ .

In this way the values of  $k$  are obtained for several wave-lengths shorter than 3300 Å. For practical reasons which will be dealt with in § 3 (b), it was found inconvenient to photograph wave-lengths longer than 3300 Å, and so to obtain points on the straight part of the  $k - \lambda^{-4}$  curve. We therefore measure the absorption coefficients of the atmosphere for green light and for red light by means of a visual photometer. The sun's light passes through a rectangular opening, an image of which is thrown by a lens on to a white screen. Alongside of this image is that of a similar aperture in a diaphragm, illuminated by an electric lamp. A variable resistance controls the voltage on the lamp, which is measured by a voltmeter. A movable filter, transmitting either the red or the green, is placed between the eye and the screen, and the voltage on the lamp is adjusted till the patches of light from lamp and sun are of equal brightness. Thus the voltage  $V$  is a measure of the intensity  $I$  of the sun's light. The photometer is calibrated, so that the value of  $I$  can be expressed in terms of  $V$ ,\* and a series of values of  $\log I$  for wave-lengths about 6000 and 5000 Å are obtained, and plotted against  $\sec z$  in the same way as for the ultra-violet.

The absorption coefficients are thus obtained for these two wave-lengths; they are equal to  $\delta + \beta_{5000}$  and  $\delta + \beta_{6000}$ . The straight line in the  $k - \lambda^{-4}$  curve is drawn through the points for  $\lambda$  6000 and  $\lambda$  5000, and the point A at  $\lambda$  3264, obtained by assuming  $x = 0.3$  cm. (its mean value).  $\lambda$  3264 is the longest wave-length which is convenient for measurement, and, as will be seen from Table I, the value of  $\alpha$  for this wave-length is so small that no appreciable error is introduced by this assumption, since the maximum variation of  $x$  is about 30 per cent. on either side of its mean value of 0.3 cm.† We therefore say that

$$\delta + \beta_{3264} = k_{3264} - 0.15 \times 0.3 = k_{3264} - 0.045.$$

If it was found that for any series the amount of ozone was unusually low or high, a more nearly correct value of  $x$  could afterwards be substituted.

$\sec z$  cannot, of course, be less than 1, but, as the distance which the light travels through the atmosphere before reaching the surface of the earth is proportional to  $\sec z$ , we may extrapolate the  $\log I - \sec z$  curves to  $\sec z = 0$ , and find what is the value of  $\log I$  before the light enters the atmosphere. This value is denoted by  $\log I_0$ .

\*  $\log I = 5.50 \log V$  for red.

$\log I = 6.06 \log V$  for green. See § 3 (c).

† See § 6.

In a similar way, by extrapolating the  $k - \lambda^{-4}$  curve to meet the  $k$  axis, we find  $\delta$ , the coefficient of the haze, or large particles, which scatter all wave-lengths alike.

§ 2 (c). *Calculation of Ozone from One Photograph (Short Method).*—For any wave-length we have

$$\log I_0 - \log I = (\beta + \delta + \alpha x) \sec z,$$

and for any second wave-length

$$\log I_0' - \log I' = (\beta' + \delta + \alpha' x) \sec z.$$

Therefore

$$x = \frac{(\log I_0 - \log I_0') - (\log I - \log I') - (\beta - \beta') \sec z}{(\alpha - \alpha') \sec z}.$$

Thus  $\delta$  is eliminated, and we can calculate the value of  $x$  from one photograph, if we assume a value for  $(\beta - \beta')$ , and that  $\log I_0 - \log I_0'$  is constant.

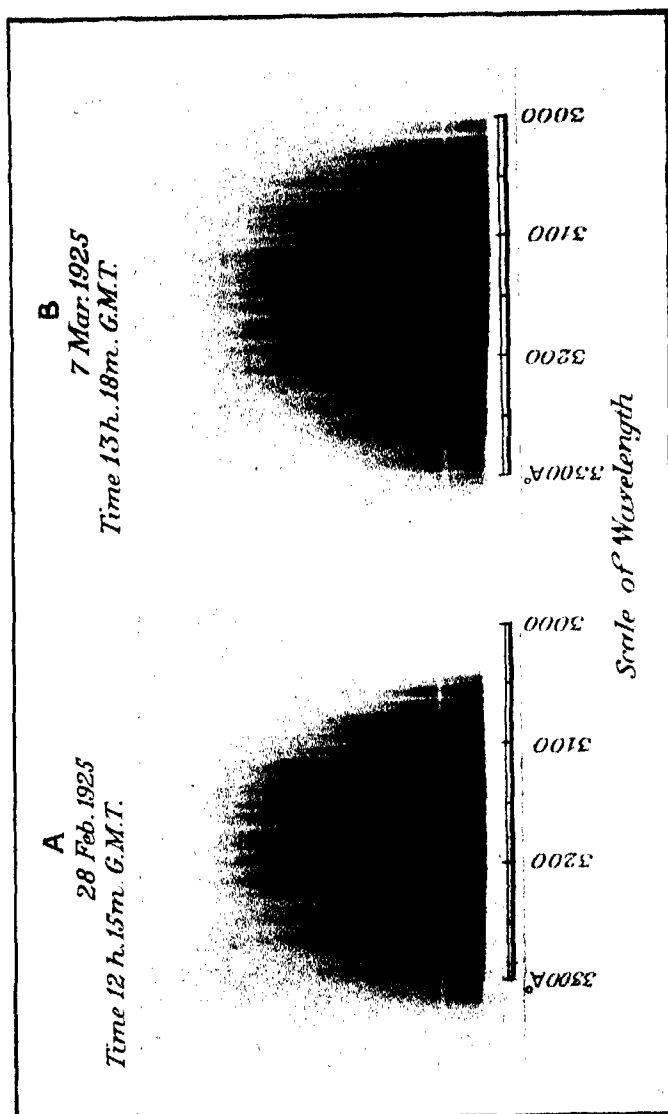
The basis of this method is, of course, the measurement of the difference between the absorptions undergone by the two wave-lengths.  $\alpha$  increases very rapidly for wave-lengths less than 3050 Å, so that it is an advantage to use two wave-lengths as far apart as possible, in order that  $\log \frac{I_0}{I} - \log \frac{I_0'}{I'}$  may be large compared with  $\beta - \beta'$  and with the errors of measurement; but, on the other hand, the shorter wave-lengths are completely cut off earlier than the longer, and we want to be able to obtain measurements at large values of  $\sec z$ .

If one wave-length is at the edge of the absorption band, where  $\alpha$  is small, the longest wave-length which gives sufficient accuracy as the second of the pair, and is convenient for measurement, is 3062; this is obtained as far as  $\sec z =$  about 2.5, i.e. from February till November.

The values of  $\alpha$  used are given in Table VI.

For the values of  $\beta$  we have taken those calculated from Rayleigh's formula on the assumption that the scattering is due to the air, the surface pressure being 1012 mb.

Plate 4 shows enlargements of two spectra, both taken with the sun at approximately the same altitude. On February 28 the amount of ozone was 0.370 cm., and on March 7 it was 0.245 cm. It will be seen that although the longer wave-lengths which are not absorbed by ozone are stronger on February 28, the shorter wave-lengths are much weaker owing to the greater amount of ozone.



Photographs on days with much and little ozone present.



## § 3. APPARATUS.

§ 3 (a). *The Spectrograph.*

It was thought desirable to avoid the use of a heliostat, and therefore it is necessary to work out of doors. It was therefore impossible to use two spectrographs at right angles, as Fabry and Buisson did, to eliminate scattered light, as these would not form a portable apparatus. A spectrograph was required which would give a dispersion of not less than  $15 \text{ \AA}$  per mm., would be convenient for use out of doors, and could be adapted so that all undesired light was removed. This latter point is always a difficulty in ultra-violet solar spectroscopy (*see* § 3 (b)).

A spectrograph to suit our requirements was not available, and one was therefore made.

The Féry type was considered most suitable because it gives an apparatus of more convenient shape than the one- or two-prism type, in which the light is turned through approximately  $45^\circ$  or  $90^\circ$ ; also because it has the minimum number of surfaces at which scattering can take place, and the lines are straight and not curved. It has, however, the disadvantage of small aperture.\* The lens, prism, and wedge (*see* § 3 (c)) are of quartz. The spectrograph is designed to give uniform illumination along the whole length of the lines on the plate.

The plate ( $12 \times 9$  cms.) is held in a metal plate-holder which slides between guides. The exposures are given by an electric shutter, worked by a current carried from the laboratory on overhead wires to the spectrograph out of doors. A pendulum in the laboratory makes contact every second, and an exposure of any whole number of seconds can be given by means of a bell-push attached to the spectrograph.

The spectrograph is carried on an alt-azimuth mounting, and is quite free to move, being held in position by hand during exposure.

A view-finder on the top of the spectrograph enables it to be pointed at the sun with sufficient accuracy, and it has been verified that no error of pointing likely to be made will result in any appreciable change of illumination.

Sec  $z$  is measured by means of an arm carrying a spirit-level, pivoted at the side of the spectrograph. During exposure the arm is turned so that it is horizontal, and the value of sec  $z$  is read off a scale fixed to the spectrograph.

\* We are indebted to Prof. T. R. Merton, F.R.S., for his advice in selecting the most desirable form of spectrograph.



§ 3 (b). *Elimination of Scattered Light.*

One of the greatest difficulties in photographing the extreme ultra-violet part of the sun's spectrum is the fogging of the plate by scattered light from the longer wave-lengths. The intensity of the shortest wave-length is extremely small compared with that of the visible and near ultra-violet, so that, unless great precautions are taken, light scattered from the surfaces of lenses and prisms swamps that which it is desired to use. Ultra-violet light is scattered much more than visible light, so that the fogging is greater than might be expected if the prism is viewed by the eye. It is impossible to make the optical system perfect enough, and some means have to be employed to remove radiation of all wave-lengths except those which are to be used.

Fabry and Buisson used two dispersions at right angles. This requires a rigid apparatus in the laboratory, together with a heliostat, the use of which we desired to avoid. It was found, however, that a suitable filter could be made of a mixture of bromine vapour and chlorine contained in a tube with quartz ends. Bromine vapour absorbs strongly from the green to about 3600 Å, and chlorine absorbs wave-lengths shorter than 3600, with a maximum at about 3400, becoming more transparent again for shorter wave-lengths.

Peskov\* has described a method for making a light-filter of bromine and chlorine for any desired part of the ultra-violet by calculation, but we found it more convenient to obtain the best amounts of the two gases by trial. Bromine was found by trial to have relatively small absorption beyond about 3600 Å, so that it does not affect the intensity of the radiation with which we are dealing. The amount of bromine required is, therefore, the maximum which it is possible to have; and this is limited by the lowest temperature at which the apparatus is to be used. The filter must remain constant, so that no bromine can be allowed to condense, and the amount required is such as will not produce saturation at the lowest working temperature (about 0° C.).

The amount of chlorine required is that which will make  $\lambda$  3350 and  $\lambda$  2950 about equally dense on the plate for the smallest values of  $\sec z$ . The intensity of the radiation which reaches the earth decreases very rapidly with  $\lambda$  in this region, owing chiefly to absorption by ozone, and if there is not enough chlorine, the ratio of the photographic intensity of the longest wave-lengths to that of the shortest which we use is too great. The chlorine equalizes matters in this respect by absorbing the longer wave-lengths of our region more than the shorter. If there is too much chlorine, the long wave-length end of this part

\* N. P. Peskov, 'Journ. Phys. Chem.,' vol. 21, p. 386 (1917).

of the spectrum is completely cut off. The correct amount of chlorine was obtained by trial.\*

As  $\sec z$  increases, the absorption by ozone cuts off the short wave-lengths, and the wave-length of maximum intensity increases.

It is, of course, necessary that the vessel in which the gases are contained should have ends of quartz, not glass, and that these ends should be as perfect optically as possible. It was found most suitable to have the whole tube made of transparent silica with optically worked ends.

### § 3 (c). *Wedge, Standard Lamp, Photometer, etc.*

The wedge, which consists of carbon in a gelatine film between quartz plates, was made by Messrs. Ilford. It was designed to give a ratio of  $10^{3.6}$  for the intensities transmitted at the top and bottom of the 2.5 cm. image at  $3000 \text{ \AA}$ . The wedge constants are determined by measuring the change in the ordinate,  $y$ , produced by a known change in the intensity of the radiation. Thus, if we know that a change of intensity in the ratio  $1 : a$  produces a change of  $b$  cms. in  $y$ , then

$$Kb = \log a, \quad \text{or} \quad K = \frac{\log a}{b}.$$

The sun's light is cut down in a known ratio by a metal disc, perforated with small holes, which is rotated in front of the spectrograph lens.† Photographs of the sun are taken alternately with and without the disc, the difference of the mean ordinates for the two sets of images giving the change  $b$ , due to the known change in the intensity of the light.

Great difficulty was found, owing to the variability of the atmosphere, but no laboratory source of ultra-violet light was available which would remain constant. Finally, the following values were adopted :—

$\lambda$ ...	3264	3232	3095 to 2978 $\text{\AA}$
$K$ ...	1.17	1.21	1.29 per cm.

$K = 0.65$  per cm. for visible wave-lengths.

The visual photometer was calibrated in a similar way by measuring the change of voltage corresponding to a known change in intensity, for the relation between brightness and voltage is of the form  $I = V^n$ .

Therefore,  $\log (I_1/I_2) = n \log (V_1/V_2)$ ,

whence  $n$  can be found.  $n = 5.50$  for the red, and  $6.06$  for the green filter used.

\* It was found that special precautions were necessary when filling the bromine and chlorine tubes, to ensure purity and dryness.

† A sector wheel must be avoided, on account of the intermittency effect and the fact that it varies the time of exposure and not the intensity.

We hoped at first to have for the standardizing image the spectrum of a half-watt lamp with a quartz window, so that each wave-length measured could be compared with the same wave-length on the standard, and a lamp was made for this purpose. It was found, however, impossible to get enough light of the required wave-lengths, and the plates are now exposed to a uniform light of wave-lengths about  $3600 \text{ \AA}$ . The light from the lamp, after passing through a piece of ultra-violet glass, falls on a strip of opal glass by which it is reflected to the plate, only a narrow strip of which is exposed. The lamp is run on a lower voltage than it normally takes; the voltage is regulated by a rheostat and voltmeter. Exposures are made by an electrically worked Thornton-Pickard shutter.

The plates are measured by means of an electric photometer. The photometer\* consists of a potassium cell, illuminated alternately by each of two beams of light from a lamp, one of which passes through the plate and the other through a movable wedge. The current passed by the cell is measured by an electrometer and a high-resistance leak. The plate rests on a travelling stage, and the distance from the zero line to the point at which the density is equal to the proper density on the wedge (as previously determined from the standard patch) is measured by the movement of the plate. The image of the photometer lamp, which has a short straight filament, is focussed on the plate by a microscope objective mounted in a tube. The width of the image is about  $1/20 \text{ mm.}$ , which is slightly less than the width of the lines on the plate.

#### § 4. RESULTS OF SERIES.

Nine good series were obtained during the summer of 1925. It is only during the time when the value of  $\sec z$  is less than  $1.5$  at noon (*i.e.* from the beginning of April to the beginning of September) that it is worth while to take series. The largest value of  $\sec z$  at which enough light is obtained for measurements to be made is  $3$ , and even at this value the shortest wave-length obtainable with 30 seconds exposure on clear days is  $3086 \text{ \AA}$ . A  $\sec z$  range of  $1.5$  is the least which it is thought worth while to have.

In fig. 1 are shown some of the  $\log I - \sec z$  curves for the series of June 4. The tangents of the angles which these straight lines make with the  $\sec z$  axis are tabulated under the heading  $k$  in the first column of Table II. These figures are plotted on a  $\lambda^{-4}$  scale in fig. 2. The values of  $\delta$ ,  $\beta$  and  $\alpha x$  are indicated in the figure, and appear in Table II, together with the values of  $\alpha$

\* See 'Photographic Photometry,' referred to previously.

calculated from Fabry and Buisson's formula. The straight line giving  $(\beta + \delta)$  is, as explained above (§ 3 (b)), drawn through the points at  $\lambda$  6000 and 5000 Å, and the point A at  $\lambda$  3264 obtained by assuming  $x = 0.3$  cm.

Table II.—Results of Series of June 4 (Morning).

$\lambda$ .	$k$ .	$\beta$ .	$\alpha x$ .	$\alpha$ .	$x$ .	$\log I_0$ .
3264 .....	0.38	0.29	—	—	—	1.57
3232 .....	0.43	0.30	—	—	—	1.86
3095 .....	0.77	0.35	0.36	1.35	0.269	2.78
3086 .....	0.83	0.36	0.42	1.50	0.283	2.94
3062 .....	1.01	0.37	0.59	2.05	0.287	3.00
3052 .....	1.055	0.37	0.63	2.33	0.270	3.10
3036 .....	1.23	0.38	0.80	2.88	0.278	3.11
3022 .....	1.38	0.39	0.94	3.44	0.274	3.03
3015 .....	1.46	0.39	1.02	3.75	0.271	3.03
2997 .....	1.76	0.40	1.31	4.75	0.277	3.17
2978 .....	2.13	0.41	1.67	6.03	0.276	3.26

$$\delta = 0.05.$$

It will be seen that in fig. 2 the points at  $\lambda$  3095 and  $\lambda$  3052 lie distinctly below the smooth curve. This is probably due to the presence of irregularities in the absorption band of ozone, as the same effect is observed in all series.\*

The last column in Table II gives the values of  $\log I_0$ , obtained by extrapolating the curves of fig. 1 to  $\sec z = 0$ . It should be particularly noted that these values are not comparable with each other, as they depend on the amount of absorption undergone by each wave-length in the apparatus, and the plate sensitivity; they are merely the values of  $Ky$  which would have been obtained if photographs had been taken with our spectrograph and bromine-chlorine filter at a point outside the atmosphere. When it is found, as it often is, that the series is very irregular, owing to changes in the atmosphere, we subtract from the value of  $\log I$  for each wave-length, the corresponding value for  $\lambda$  3264, which is the longest wave-length convenient for measurement. Changes in haziness, which reduce all wave-lengths in the same proportion, are thus eliminated. This is the procedure adopted by Fabry and Buisson in their original measurements, and results in a great improvement in the curves. The values of  $k - k'$  (where  $k'$  is the absorption coefficient for  $\lambda$  3264) are thus obtained, and subtracting the value of  $\beta - \beta'$  calculated from Rayleigh's formula we get  $x(\alpha - \alpha')$ , and hence  $x$  for each wave-length. We also get  $\log I_0/I_0'$ .

\* In a recent paper—'Publ. Inst. of Technology,' Mass., vol. 60, No. 56—Fabry gives detailed absorption coefficients for ozone for wave-lengths larger than 3060 Å, but unfortunately these are all longer wave-lengths than those we require.

The results of the nine series may be summarised as follows :—

(1) The values of ozone from different wave-lengths in any one series agree well, and their slight discrepancies indicate that the absorption coefficients used are not correct. When the amount of ozone given by each wave-length is expressed as a percentage of the mean for the series, each wave-length shows a remarkable consistency through all the series (see Table III).\*

Table III.—Values of  $x$  expressed as Percentages of Means for  $\lambda\lambda$  3095–15.  
June, 1925.

$\lambda$ .	2nd.	3rd.	4th.		5th.	10th.	11th.	15th.		Mean.
			a.m.	p.m.				a.m.	p.m.	
3095 .....	95	98	97	97	98	100	107	99	99	98.9
3086 .....	102	106	103	106	107	101	109	100	109	104.8
3082 .....	105	104	104	106	103	103	101	103	105	103.7
3052 .....	98	97	98	95	94	93	96	95	96	95.8
3036 .....	103	101	101	98	99	101	97	99	96	99.4
3022 .....	96	100	99	98	104	99	94	99	96	98.3
3015 .....	103	95	98	100	97	100	96	98	97	98.2
2997 .....	—	99	100	—	—	—	92	99	94	96.8
2978 .....	—	111	—	99	—	—	94	101	115	104.0

The figures below the line in each series were obtained from points extending over a range of  $\sec z$  of less than 1.

This is strong proof that the absorption is due only to ozone. The final column in Table III indicates approximately how much the values of  $\alpha$  are in error, assuming the mean for all wave-lengths to be correct; for instance, that for  $\lambda$  3052 should be multiplied by about  $\frac{95.8}{100}$ . The corrected values of  $\alpha$  are given in Table IV.

Table IV.—Corrected Values of  $\alpha$ .

$\lambda$	...	3095	3086	3062	3052	3036	3022	3015
$\alpha$	...	1.33	1.57	2.13	2.23	2.86	3.38	3.68

The fact that the different wave-lengths do not agree in the values of  $x$  which they give, might be due to errors in the wedge constant  $K$ , but there is no indication in the measurements of  $K$  that the absorption of "neutral"

\* In calculating the mean, only  $\lambda\lambda$  3095–3015 are taken into account, in order that the series may be comparable. Some earlier series do not agree well with the ones shown, because the sun's altitude was too small to give sufficient points for accuracy.

gelatine film varies in an irregular manner with wave-length, whereas we know that ozone has well-marked bands.\*

(2) In the two cases in which two series have been obtained on the same day, the amounts of ozone given by the morning and afternoon series agree well, although  $\beta$  and  $\delta$  are not the same.

(3) The values of  $\log I_0$  are fairly consistent, especially when differences are taken instead of absolute values. The values of  $\log I_0 - \log I_{0_{\text{sun}}}$  are given in Table V.†

Table V.—Values of  $\log I_{0_\lambda} - \log I_{0_{\text{sun}}}$ . June, 1925.

$\lambda$ .	2nd.	3rd.	4th.		5th.	10th.	11th.	15th.		Mean.
			a.m.	p.m.				a.m.	p.m.	
3232 .....	0.23	0.27	0.29	0.28	0.26	0.27	0.29	0.30	0.28	0.28
3095 .....	1.18	1.24	1.21	1.24	1.25	1.24	1.29	1.25	1.24	1.24
3086 .....	1.32	1.39	1.37	1.43	1.41	1.37	1.41	1.41	1.42	1.39
3062 .....	1.38	1.43	1.43	1.49	1.44	1.41	1.40	1.43	1.44	1.43
3052 .....	1.46	1.50	1.53	1.55	1.51	1.46	1.54	1.50	1.50	1.51
3036 .....	1.49	1.55	1.54	1.56	1.56	1.51	1.50	1.53	1.48	1.53
3022 .....	1.34	1.48	1.46	1.51	1.56	1.40	1.38	1.45	1.41	1.44
3015 .....	1.34	1.41	1.46	1.55	1.49	1.44	1.43	1.46	1.43	1.45

The figures below the line in each series were obtained from points extending over a sec  $z$  range of less than 1.

## § 5. ACCURACY AND SOURCES OF ERROR.

### § 5 (a). Errors in $k$ , $x$ and $\log I_0$ found from Series.

§ 5 (a) (i) *Changing Atmosphere*.—Changes in the atmosphere are the greatest source of error. If the absorption coefficient changes during a series, it is not at first obvious what meaning should be given to the observed values. It can, however, be shown that if the change is uniform with time, the points obtained will lie on approximately straight lines, whose slopes give values of  $k$  which were the true ones when  $\sec z = \infty$ , i.e. at sunrise and sunset.

If the change were due to haze alone,  $\beta$  and  $x$  remaining constant, all wave-lengths would be affected equally, and even if the points did not lie on straight lines, the slopes of all the mean lines would be altered by equal amounts; all the points on the  $k - \lambda^{-4}$  curve would then be raised or lowered equally, and the result would be an error in  $\delta$ , but not in  $\beta$  or  $x$ . Similarly, a change

\* Fowler and Strutt, 'Roy. Soc. Proc.,' A, vol. 93, p. 577 (1917).

† See § 5 (a) (i).

in  $\beta$  during the series will alter the slope of the straight part of the  $k - \lambda^{-4}$  curve, and therefore the value deduced for  $\beta$ , but not  $\delta$  or  $x$ . A change in the amount of ozone will likewise affect the value of  $x$  alone.

The two series of June 4 give an interesting illustration of a varying atmosphere. The amounts of ozone are practically the same for morning and afternoon, but  $\beta$  and  $\delta$  are greater for the afternoon. The afternoon values of  $\log I_0$  are greater than the morning ones, which indicates that the change was a gradual one, and did not take place during the interval at noon; and the smoothness of the  $\log I - \sec z$  curves shows that the change was fairly regular.

It is difficult to estimate the probable error in  $\log I_0$  due to changes in the atmosphere, but we can get some idea of it in the following way:—

Suppose that the true value of  $\log I_0$  is given by A (fig. 3), and that when  $\sec z = 3.0$  the value of  $k$  is given by AB. Then if  $k$  remained constant, the points would lie on AB. Suppose that  $\delta = 0.10$  and that it increases ( $\beta$  and

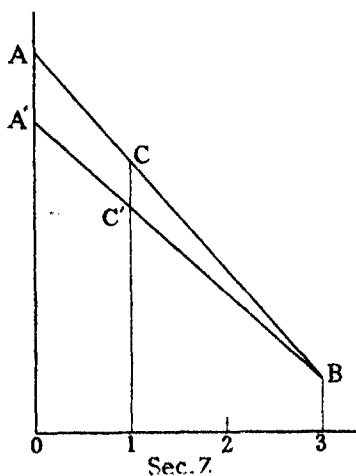


Fig. 3.

$x$  being constant) in such a way that the points lie on the line  $BC'$ , and that by noon, when  $\sec z$  is nearly 1.0, it has changed by 0.02, or 20 per cent. of its former value. Then  $CC' = 0.02$ , and the value of  $\log I_0$  obtained by extrapolation will be  $A'$ ,  $AA'$  being equal to 0.03. We may thus expect considerable inaccuracy in our values of  $\log I_0$ , but as explained above, the differences should show much less error. It is evident from fig. 3 that  $AA'$  is the same whatever the value of  $k$ . If  $\delta$  increases uniformly during the whole day, the mean of  $\log I_0$  for morning and afternoon series will be the correct value. Similar considerations apply to changes in  $\beta$  and  $x$ . The importance of

correct values of  $\log I_0$  will be discussed in § 5 (b) (iii).

§ 5 (a) (ii) *Other Absorbing Gases in the Atmosphere.*—If there were another gas in the atmosphere, which absorbed at any of the wave-lengths which we measure, the absorption coefficients for these wave-lengths would be abnormally large, and the values of  $x$  deduced from them would not be in agreement with the rest. It is therefore unlikely that there is such a gas, although there are certain inconsistencies in Table III (e.g. on June 11).

§ 5 (a) (iii) *Wedge Constant*.—Since all the observed values of  $\log I$  are proportional to  $K$  (equation (4)), an error in  $K$  would produce a proportional error in  $k$ . Consequently different wave-lengths would be affected differently (see § 4), and part of the discrepancy between the values of  $x$  given by different wave-lengths may be due to this cause. It is probable, however, that the absorption coefficient of the material of which the wedge is made increases regularly towards the shorter wave-lengths, so that, as our values of  $K$  lie on a smooth curve, no irregular effect is to be expected.

The observed values of  $\log I_0$  are, of course, directly proportional to  $K$ .

§ 5 (a) (iv) *Plate Errors*.<sup>\*</sup>—When the values of  $\log I_{3264}$  are subtracted before plotting, the irregularities of  $\delta$  are eliminated, and almost those of  $\beta$ , which should appear progressively greater for shorter wave-lengths. Any remaining irregularities may be put down to errors in the plate, and a study of the  $\log I - \sec z$  curves from this point of view gives an indication of the size of such errors. As an example, in the series illustrated in fig. 1, at  $\sec z = 3.00$ ,  $\lambda 3086$  is too high by 0.03.

It is found that the probable error in  $\log I$  is 0.005, which is equivalent to about 1 per cent. in  $I$ .

If we assume that the atmosphere remains constant during a series, the probable error in the observed values of  $k$  due to errors of the plate will be about 0.005, with a  $\sec z$  range of 2. The resulting error in  $x$  depends on  $\alpha$ , and for  $\lambda 3052$  is about 0.002 cm., or less than 1 per cent., since  $x = 0.3$  cm. We do not attach much weight to those values which are obtained from a  $\sec z$  range of less than 1.

#### § 5 (b). *Errors in amount of Ozone calculated from Single Photographs.*

§ 5 (b) (i) *Errors in  $\beta$* .—For the values of  $\beta$  we have taken those calculated from Rayleigh's formula on the assumption that the scattering particles are the air molecules at 760 mm. pressure.  $\beta$  is, of course, proportional to the pressure, so that a change of 3 per cent. in either direction may be expected from this cause. The error introduced by wrong values of  $\beta$  is proportional to  $\frac{\beta - \beta'}{\alpha - \alpha'}$ , on this account, as mentioned above, it is advisable to use wave-lengths as widely separated as possible. The value of  $\frac{\beta - \beta'}{\alpha - \alpha'}$  for  $\lambda\lambda 3232$  and 3052, one

<sup>\*</sup> For a study of the inaccuracy due to irregularity of the plate, and also a description of the best methods of development, etc., see 'Photographic Photometry,' to which we have already referred.



of the pairs which we have used, is 0.04, so that a 25 per cent. change in  $\beta$  from its calculated value would introduce an error of 0.01 cm. in  $x$ . We do not think that such a change ever takes place;  $\beta$  cannot, of course, have much less than its calculated value, but it may be greater owing to the presence of other particles small enough to scatter according to the  $\lambda^{-4}$  law. The results of the series show  $\beta$  changes.

§ 5 (b) (ii) *Photographic Errors.*— $\alpha - \alpha'$  for  $\lambda\lambda$  3232 and 3052 is 2.03, so that an error of 0.03 in  $\log I - \log I'$  produces an error of 0.01 cm. in  $x$ , at  $\sec z = 1.5$ . Considerations of the accuracy of the plate show that the probable error in  $x$  due to this cause is about 0.002 cm.

§ 5 (b) (iii) *Errors in Log  $I_0$ .*—If the adopted values for  $\log I_0 - \log I_0'$  are wrong, systematic errors will be introduced. For if the value used for any pair of wave-lengths be too great by an amount  $i$ , then the calculated value of  $x$  will be too great by  $i/(\alpha - \alpha') \sec z$ ; thus, a regular change with  $\sec z$  will be introduced, the error being inversely proportional to  $\sec z$ . The fact that no such effect is observed shows that our values of  $\log I_0/I_0'$  cannot be far wrong.

§ 5 (b) (iv) *Changes in Sun.*—It is, of course, possible that the relative intensities of two wave-lengths emitted by the sun may vary, and some of the observed irregularities may be due to this cause. It can be shown from Planck's formula for radiation that if the sun radiates as a black body at  $6000^\circ$ , a change of  $500^\circ$  will result in a change of 0.04 in  $\log I_0 - \log I_0'$  for  $\lambda\lambda$  3232 and 3052, which would give rise to an error in ozone of 0.01 cm. at  $\sec z = 2$ , and changes in the gases of the photosphere may give greater variations than this.

§ 5 (b) (v) *Errors in  $\alpha$ .*—If the values of  $\alpha - \alpha'$  are still wrong, all the values of  $x$  will be wrong in the same proportion. This not a serious matter, and can easily be further adjusted if experience shows it to be necessary.

§ 5 (b) (vi) *Wedge Constant.*—The amount of absorption undergone by any wave-length is given by

$$\log I_0 - \log I = k \sec z = K (y_0 - y), \quad (5)$$

where

$$Ky_0 = \log I_0 \text{ (cf. § 5 (a) (iii)).}$$

Thus the true value of  $x$  is (equation (5))

$$\frac{K(y_0 - y) - K'(y'_0 - y') - (\beta - \beta') \sec z}{(\alpha - \alpha') \sec z}.$$

The observed value is

$$\frac{pK(y_0 - y) - qK'(y'_0 - y') - (\beta - \beta') \sec z}{(\alpha - \alpha') \sec z},$$

where  $pK$  and  $qK'$  are the adopted values of  $K$ .

Therefore error

$$= \frac{(p-1)K(y_0-y) - (q-1)K'(y'_0-y')}{(\alpha-\alpha')\sec z}$$

$$= \frac{(p-1)k - (q-1)k'}{\alpha-\alpha'}.$$

Thus an approximately constant error is introduced, since  $k$  and  $k'$  do not vary greatly. Of course, the corrections applied to  $\alpha$  depend on the adopted values of  $K$  (§ 4), but these are, as a matter of fact, small.

The small differences between the mean value of the ozone for different wave-length pairs may perhaps be partly accounted for in this way.

§ 5 (b) (vii) *Scattered Light*.—A certain amount of light is unavoidably scattered inside the spectrograph, most of this being naturally of those wave-lengths which are strongest in our spectrograms. Therefore the ratio of the total scattered light to the useful light of any one wave-length varies with  $\sec z$ , as the wave-length of maximum intensity varies. Nevertheless, it has been found that the total scattered light is negligible compared with the intensity of any of the wave-lengths which we use.

§ 5 (b) (viii) *Other Absorbing Gases in Atmosphere* (cf. § 5 (a) (ii)).—It is also possible that other gases than ozone absorb in the region of the spectrum with which we are dealing. None of the other constituents of the atmosphere are known to have such an absorption, but if this were the case the values of the ozone calculated from different pairs of wave-lengths would not agree.

The amount of ozone was calculated from equation (5), using the constants obtained from the series (Tables IV and V), for five pairs of wave-lengths, or as many as could be measured in the photographs, for a large number of days. The results for the month of May are shown in fig. 4. The different curves agree well, and this is additional proof that the absorption is, a matter of fact, as due to ozone, and that the errors are not large. Nevertheless, it is possible that certain anomalies in the behaviour of the curve in fig. 5 may be explained in this way.

§ 5 (b) (ix) *Photometer Measurements*.—The measurements of the plates are very accurate, and can usually be repeated to within 0.05 mm. Moreover, as the discrepancy between two independent sets of readings is mainly due to errors in setting on the zero line, or in estimating the mean density of the background near the image or of the standard strip, all wave-lengths are affected by the same amount, and the resulting error in  $x$  is negligible.

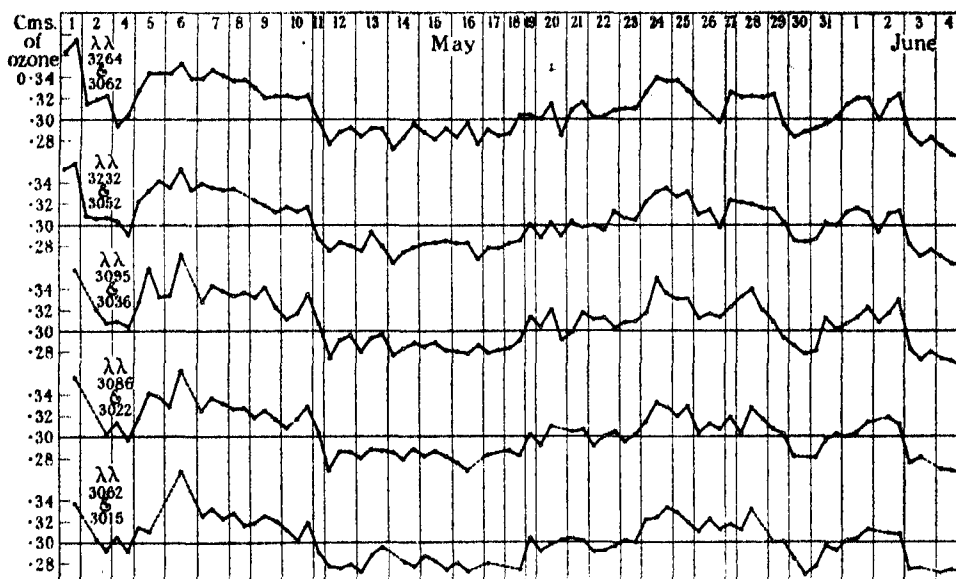


Fig. 4.

Finally, we estimate that the probable error of any one determination of the amount of ozone is not greater than 0.005 cm., excluding systematic errors, such as those in  $\alpha$ .

Two independent measurements of twelve images gave the following values for the ozone :—

First measurement, 0.251, 0.249, 0.239, 0.233, 0.244, 0.240,

Second measurement, 0.251, 0.249, 0.238, 0.233, 0.244, 0.240,

First measurement, 0.234, 0.228, 0.214, 0.212, 0.209, 0.206.

Second measurement, 0.235, 0.229, 0.216, 0.212, 0.212, 0.205.

#### § 6. VARIATION OF OZONE DURING 1925.

The mean values of the ozone expressed as the thickness in cms. of an equivalent layer of pure ozone at N.T.P., for every day during 1925 on which photographs could be taken, are tabulated in Table VI, together with the barometric pressure at Oxford, and the sunspot numbers.\*

\* See § 7 (f).

The ozone and pressure daily values are plotted in fig. 5; the pressure is plotted so that it decreases upwards, in order to bring out the connection between it and the ozone. The series of horizontal lines marked A and C above the curves refers to the weather conditions; the upper ones (C) mark the occurrence of cyclones, the lower (A) of anticyclones; dots mean that the conditions were not well defined.

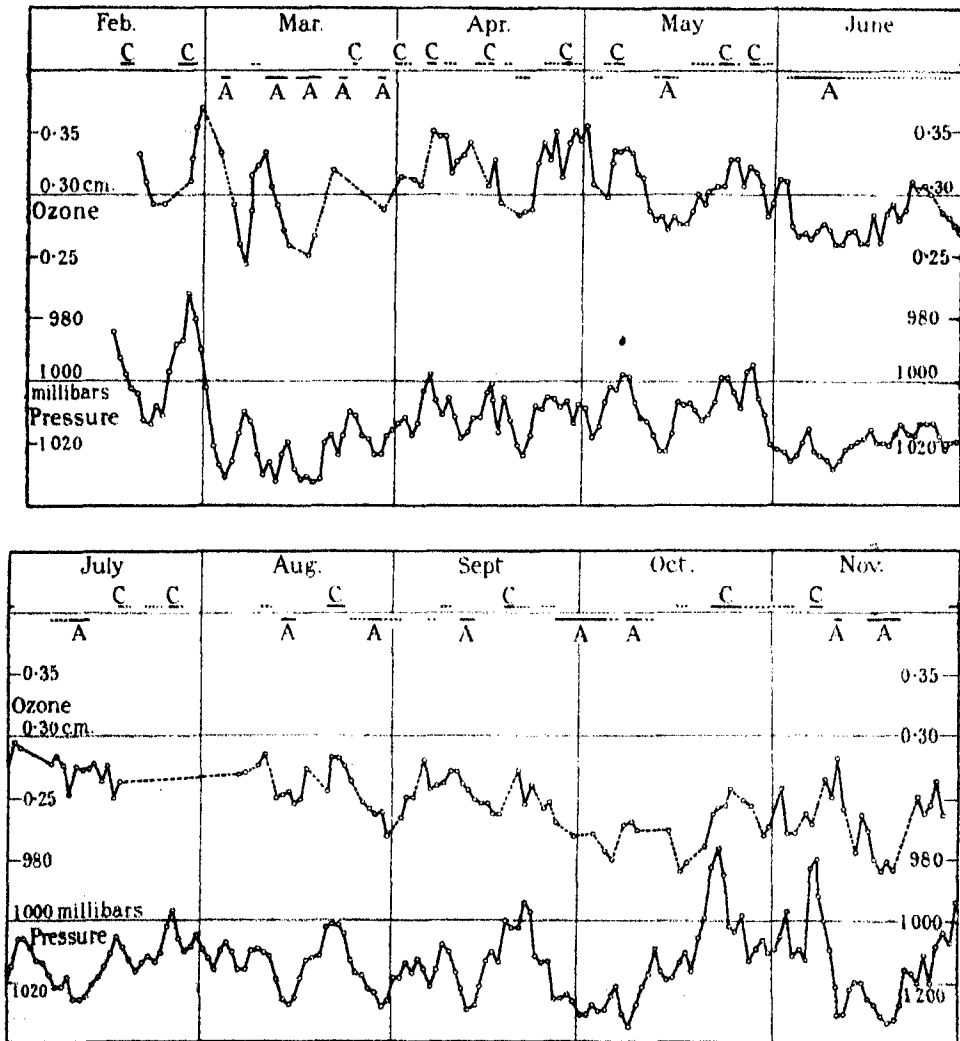


Fig. 5.—Daily Values of Ozone and Pressure.

Table VI.—1924.

Date.	Average time.	Ozone. Cms.	Surface pressure. Mb.	Date.	Average time.	Ozone. Cms.	Surface pressure. Mb.
Aug. 18 .....	p.m.	0.301	994	Sept. 10 .....	{ a.m.	0.253	1012
" 19 .....	N.	0.302	999	" 10 .....	{ p.m.	0.231	1014
" 20 .....	N.	0.289	998	Oct. 6 .....	p.m.	0.244	1006
" 22 .....	p.m.	0.262	1002	" 8 .....	p.m.	0.251	998
" 23 .....	a.m.	0.279	1003	" 14 .....	p.m.	0.226	1031
" 27 .....	N.	0.262	1014	" 23 .....	N.	0.236	1030
Sept. 1 .....	p.m.	0.229	1016	" 24 .....	a.m.	0.236	1026
" 3 .....	p.m.	0.247	1023				

1925.\*

Day.	February.				March.			
	Average Time.	Ozone.	Surface Pressure. Mb.	Sunspot Number.	Average Time.	Ozone.	Surface Pressure. Mb.	Sunspot Number.
1	—	—	—	—	—	—	1002	—
2	—	—	—	—	—	—	1021	8
3	—	—	—	—	a.m.	0.333	1027	7
4	—	—	—	—	—	—	1031	—
5	—	—	—	—	p.m.	0.291	1026	0
6	—	—	—	—	N.	0.260	1017	—
7	—	—	—	—	p.m.	0.244	1010	—
8	—	—	—	—	{ a.m.	0.287	1006	0
9	—	—	—	—	{ p.m.	0.315	1013	
10	—	—	—	—	N.	0.323	1024	0
11	—	—	—	—	a.m.	0.333	1030	0
12	—	—	—	—	p.m.	0.305	1026	9
13	—	—	—	71	N.	0.291	1032	17
14	—	—	984	—	p.m.	0.271	1024	17
15	—	—	993	49	N.	0.259	1020	—
16	—	—	998	15	—	—	1029	—
17	—	—	1002	31	—	—	1032	20
18	N.	0.338	1004	12	N.	0.250	1031	28
19	a.m.	0.310	1013	36	N.	0.266	1033	34
20	p.m.	0.292	1014	13	—	—	1032	32
21	—	—	1008	11	a.m.	0.320	1020	24
22	p.m.	0.293	1011	—	—	—	1018	17
23	—	—	997	14	—	—	1024	—
24	—	—	988	13	—	—	1018	—
25	—	—	987	0	—	—	1010	—
26	{ a.m.	0.310	974	7	—	—	1011	—
27	{ p.m.	0.329	970		—	—	1018	—
28	a.m.	0.353	980	0	—	—	1019	43
29	p.m.	0.370	990	14	—	—	1024	36
30	—	—	—	—	p.m.	289	1024	34
31	—	—	—	—	—	—	1018	24
					—	—	1016	22

\* See also pp. t83-t.

Table VI.—1925—continued.

Day.	April.				May.			
	Average Time.	Ozone.	Surface Pressure. Mb.	Sunspot Number.	Average Time.	Ozone.	Surface Pressure. Mb.	Sunspot Number.
1	N.	0.314	1014	10	a.m.	0.355	1009	19
2	—	—	1012	8	a.m.	0.308	1019	23
3	a.m.	0.312	1018	7	—	—	1015	35
4	a.m.	0.307	1014	14	p.m.	0.298	1007	35
5	—	—	1003	19	a.m.	0.325	1004	31
6	p.m.	0.352	998	17	p.m.	0.335		
7	a.m.	0.347	1006	24	N.	0.334	1003	43
8	a.m.	0.347	1011	21	a.m.	0.336	998	37
9	a.m.	0.317	1006	31	p.m.	0.334	999	34
10	a.m.	0.327	1012	—	N.	0.317	1007	43
11	N.	0.331	1019	—	a.m.	0.314	1012	39
12	a.m.	0.342	1017	52	a.m.	0.287	1013	—
13	—	—	1012	57	a.m.	0.280	1018	—
14	—	—	1012	42	a.m.	0.283	1023	27
15	p.m.	0.307	1004	35	a.m.	0.272	1023	38
16	p.m.	0.327	1003	31	N.	0.283	1017	47
17	N.	0.294	1017	42	p.m.	0.277	1007	47
18	—	—	1006	35	p.m.	0.277	1008	78
19	—	—	1012	60	a.m.	0.286	1008	83
20	p.m.	0.284	1021	—	p.m.	0.300	1010	70
21	N.	0.286	1024	40	p.m.	0.293	1013	69
22	a.m.	0.288	1018	44	a.m.	0.301	1011	74
23	p.m.	0.325	1008	36	N.	0.307	1007	71
24	a.m.	0.341	1009	—	N.	0.306	999	54
25	N.	0.327	1005	—	p.m.	0.329	999	39
26	a.m.	0.350	1006	—	p.m.	0.329	1004	32
27	a.m.	0.314	1008	—	a.m.	0.307	1009	28
28	p.m.	0.342	1007	7	p.m.	0.323	997	41
29	N.	0.351	1014	7	N.	0.319	995	40
30	a.m.	0.344	1008	16	a.m.	0.308	1006	28
31	—	—	—	—	N.	0.284	1011	17
						0.295	1021	—

## § 7. GEOPHYSICAL RESULTS.

§ 7 (a) *Annual Variation*.—Naturally no precise information regarding the annual variation can be obtained from only one year's observations, but it appears fairly certain that there is a marked yearly period, the maximum occurring in the spring, and the minimum in the late autumn; the range would appear to be about 0.15 cm. of ozone. This is in accordance with the observations of Dr. P. Götz at Arosa, who found that during 1922–23 the ultra-violet light reaching the earth's surface was a minimum in April and a maximum in December. The dates of maximum and minimum are peculiar, and not what might at first sight be expected if the variations are

Table VI.—1925—*continued*.

Day.	June.				July.			
	Average Time.	Ozone.	Surface Pressure. Mb.	Sunspot Number.	Average Time.	Ozone.	Surface Pressure. Mb.	Sunspot Number.
1	N	0.314	1022	40	N.	0.295	1015	22
2	a.m.	0.312	1023	83	a.m.	0.290	1006	28
3	N.	0.275	1026	92	—	—	1006	39
4	N.	0.266	1024	80	—	—	1009	47
5	a.m.	0.269	1020	94	—	—	1012	66
6	N.	0.264	1016	73	—	—	1014	50
7	a.m.	0.273	1023	89	p.m.	0.277	1018	48
8	p.m.	0.277	1024	118	a.m.	0.288	1022	61
9	p.m.	0.272	1026	114	N.	0.276	1022	—
10	p.m.	0.260	1029	109	p.m.	0.252	1019	43
11	a.m.	0.280	1026	102	a.m.	0.275	1026	38
12	p.m.	0.270	1022	89	N.	0.272	1026	37
13	a.m.	0.271	1021	88	N.	0.274	1025	39
14	p.m.	0.261	1020	56	a.m.	0.278	1021	20
15	N.	0.262	1019	35	a.m.	0.263	1019	21
16	N.	0.285	1016	17	a.m.	0.276	1015	41
17	a.m.	0.263	1020	8	p.m.	0.250	1011	40
18	a.m.	0.285	1020	13	a.m.	0.263	1006	31
19	p.m.	0.293	1021	7	—	—	1009	28
20	N.	0.280	1017	0	—	—	1013	35
21	p.m.	0.288	1014	0	—	—	1017	38
22	a.m.	0.311	1017	18				
23	N.	0.305	1018	14				
24	p.m.	0.308	1014	7				
25	N.	0.300	1014	12				
26	—	—	1014	11				
27	p.m.	0.287	1018	16				
28	p.m.	0.284	1022	14				
29	N.	0.276	1020	11				
30	a.m.	0.271	1020	17				

due to the varying altitudes of the sun. The annual variation is very much complicated by the superimposed variations associated with pressure changes (*see (d) and (e) below*).

§ 7 (b) *27-Day Period*.—During a period of some months (May to August) there were indications of a 27-day period such as might be associated with the period of revolution of the sun. However, if changes apparently associated with barometric pressure variations are eliminated, this periodicity largely disappears, and up to the present there seems no certain evidence of such a period, though the apparent connection with sunspots and magnetic data would indicate that such a period was not improbable.

§ 7 (c) *Diurnal Variation*.—No evidence of such a variation has been obtained. It can be shown that if there were a regular diurnal variation

Table VI.—1925—continued.

Day.	August.				September.			
	Average Time.	Ozone,	Surface Pressure. Mb.	Sunspot Number.	Average Time.	Ozone.	Surface Pressure. Mb.	Sunspot Number.
1	—	—	—	—	—	—	1019	76
2	—	—	—	—	p.m.	0.235	1019	59
3	—	—	—	—	a.m.	0.250	1014	80
4	—	—	—	—	N.	0.250	1017	73
5	—	—	1007	8	—	—	1013	60
6	—	—	1010	23	N.	0.281	1016	71
7	p.m.	0.269	1016	28	p.m.	0.257	1021	43
8	p.m.	0.270	1016	40	N.	0.260	1016	38
9	—	—	1010	56	p.m.	0.262	1008	65
10	p.m.	0.276	1009	70	a.m.	0.272	1010	47
11	a.m.	0.285	1010	57	a.m.	0.271	1017	36
12	—	—	1011	47	N.	0.260	1022	30
13	p.m.	0.250	1019	46	p.m.	0.257	1029	21
14	N.	0.252	1026	31	N.	0.249	1028	30
15	a.m.	0.254	1027	7	a.m.	0.246	1021	42
16	a.m.	0.246	1025	7	p.m.	0.246	1013	60
17	a.m.	0.249	1019	7	a.m.	0.236	1010	—
18	p.m.	0.274	1013	10	a.m.	0.236	1013	51
19	—	—	1012	28	—	—	1000	60
20	—	—	1001	24	—	—	1002	67
21	a.m.	0.255	1002	30	N.	0.271	1002	76
22	a.m.	0.283	1001	19	p.m.	0.245	994	83
23	a.m.	0.282	1001	31	p.m.	0.260	997	77
24	N.	0.277	1004	30	—	—	1011	—
25	a.m.	0.263	1013	—	a.m.	0.241	1013	76
26	—	—	1017	64	N.	0.247	1013	82
27	N.	0.246	1018	64	N.	0.230	1025	86
28	N.	0.242	1022	71	—	—	1025	77
29	N.	0.237	1023	77	—	—	1024	77
30	a.m.	0.239	1028	—	N.	0.218	1026	—
31	a.m.	0.219	1026	92	—	—	—	—

with maximum or minimum at local noon, no evidence of it would be shown, and the values found would apply to the amount of ozone present at about sunrise or sunset. This is due to the fact that in calculating the amount of ozone by the long method (*see* § 2 (a)) we must assume the atmosphere to be constant during the interval over which observations are taken, and if the conditions are changing regularly we obtain a result which would be true when the sun was on the horizon. Moreover the values of  $\log I_0$  found by the long method observations are so changed that when the amount of ozone is calculated by the short method (*see* § 2 (c)) the value would again always be equal to the true value at sunrise or sunset, whatever time the actual observation was made. We have thus no evidence that diurnal variation does not take place.



Table VI.—1925—*continued*.

Day.	October.			November.		
	Average Time.	Ozone.	Surface Pressure. Mb.	Average Time.	Ozone.	Surface Pressure. Mb.
1	—	—	1031	—	—	1009
2	—	—	1031	N.	0.258	1005
3	N.	0.221	1027	N.	0.221	997
4	—	—	1020	N.	0.222	1011
5	N.	0.207	1029	—	—	1009
6	N.	0.200	1024	N.	0.237	1013
7	—	—	1021	N.	0.228	983
8	N.	0.228	1030	—	—	986
9	N.	0.230	1034	N.	0.264	1000
10	p.m.	0.224	1027	N.	0.250	1009
11	—	—	1021	N.	0.281	1026
12	—	—	1017	N.	0.240	1030
13	—	—	1009	—	—	1022
14	—	—	1016	N.	0.205	1020
15	N.	0.224	1018	N.	0.236	1020
16	—	—	1018	N.	0.223	1025
17	p.m.	0.100	1013	N.	0.200	1027
18	a.m.	0.197	1010	N.	0.192	1031
19	—	—	1016	N.	0.198	1033
20	—	—	1005	N.	0.191	1032
21	a.m.	0.210	999	—	—	1027
22	a.m.	0.237	982	—	—	1016
23	a.m.	0.243	976	—	—	1017
24	N.	0.244	984	N.	0.251	1020
25	a.m.	0.257	1001	N.	0.237	1011
26	—	—	1003	N.	0.244	1020
27	N.	0.238	998	N.	0.263	1008
28	N.	0.235	1013	N.	0.235	1004
29	—	—	1009	—	—	1007
30	N.	0.220	1006	—	—	994
31	N.	0.226	1010	—	—	—

§ 7 (d) *Connection with Atmospheric Pressure.*—The most interesting result obtained from this series of observations is the relation shown between the variations of the amount of ozone and the pressure of the atmosphere. Since there is reason to suppose that the ozone is situated above the troposphere, one would expect the variations in the ozone to be related—if at all—to the conditions in the upper air rather than to conditions near the earth's surface. Unfortunately the information relating to the upper atmosphere is very scarce. However, the figures of Table VI show clearly that a very definite connection exists between the variations in the amount of ozone and surface pressure. Considering that it is highly probable that this connection only exists through the pressure at great heights, the agreement is as close as could be expected,

for W. H. Dines\* has shown that the correlation coefficient between the surface pressure and that at 9 km. is only 0.68. High values of ozone are associated with cyclonic, and low values with anticyclonic, conditions. Further, if instead of using the absolute surface pressure at Oxford, one takes the general pressure distribution in the neighbourhood, a closer connection is observed, and it is possible to see that, with very few exceptions, almost all changes in the amount of ozone are associated with changes in the surface pressure distribution. There appears to be a tendency for the changes in the amount of ozone to reach a maximum a day or two after the extremes of pressure, and this is quite as marked with anticyclones as with cyclones. Did this lag occur in the case of cyclones only one would suspect that it was connected with the different origins of the air currents usually found in the front or rear of a cyclone, but the fact that it occurs in anticyclones also is against this supposition.

It is of interest to note that while Fabry and Buisson's results in 1920 were mostly made in anticyclonic conditions, yet it is possible to trace the variation of ozone with pressure even in these few early observations.

There is reason to suppose that secondary depressions are frequently confined to the lower atmosphere, and that they do not extend to the stratosphere, as in the case of cyclones. In view of this it is important to notice that when well-marked secondary depressions have crossed southern England, the ozone has shown little variation, while when cyclones have followed the same course large effects in the amount of ozone have almost always been observed.

§ 7 (e) *Connection with Upper Air Conditions.*—We are greatly indebted to the Director of the Meteorological Office and Mr. L. H. G. Dines for supplying us with all the information obtained from British ballon-sondes ascents, and giving us all possible assistance. The full data are set out in Table VII. There are 19 days when comparison can be made, but unfortunately there is often considerable difference of time between the two observations, and since the ballon-sonde ascents were made from either Kew or Sealand (Chester) there is also a large difference of locality.

In fig. 6 (a) the values of the pressure at 12 kms. ( $P_{12}$ ), the pressure at the base of the stratosphere ( $P_s$ ), and the height of the base of the stratosphere ( $H_s$ ) are plotted as ordinates, while the values of the ozone are plotted as abscissæ. A diagram giving a similar comparison for the surface pressure at Oxford ( $P_s$ ) on the same days that upper air data are available is also added for comparison.

\* W. H. Dines, 'Geophysical Memoirs,' No. 18.

Table VII.—Upper Air Data.

Date.	Place.	Time.	P <sub>5</sub>	P <sub>9</sub>	P <sub>12</sub>	P <sub>14</sub>	P <sub>16</sub>	P <sub>18</sub>	T <sub>14</sub>	T <sub>16</sub>	T <sub>18</sub>	H <sub>c</sub>	P <sub>c</sub>	P <sub>c</sub>	Ozone
1924.		G.M.T.	mb.	mb.	mb.	mb.	mb.	mb.	°a.	°a.	°a.	Km.	mb.	°a.	cm.
Sept. 3	S	7.22	1023	320	203	148	108	—	215	217	—	12.7	181	217	0.247
1925.															
March 17	S	17.40	1032	310	193	140	102	74	215	213	213	11.4	212	208	0.250
.. 19	S	7.25	1032	310	195	143	105	—	221	222	—	10.9	230	216	—
.. 21	S	8.00	1018	282	179	133	97	—	223	223	—	7.5	353	221	0.320
April 14	S	17.50	1012	303	—	—	—	—	—	—	—	10.5	238	219	—
.. 15	S	7.50	1004	292	187	—	—	—	—	—	—	8.9	296	227	0.307
.. 16	S	17.59	1001	297	187	138	—	—	225	—	—	10.5	236	222	0.327
.. 21	K	15.34	1024	308	192	—	—	—	—	—	—	11.0	227	213	0.286
May 13	S	17.50	1024	311	194	141	—	—	219	—	—	11.8	202	211	0.283
.. 14	S	7.43	1023	313	197	143	106	—	222	223	—	11.5	214	215	0.272
.. 15	S	7.55	1017	311	195	143	105	—	221	223	—	11.1	223	215	0.283
June 18	S	18.30	1020	310	193	140	103	75	217	217	218	11.5	210	209	0.285
.. 19	S	17.45	1021	312	197	—	—	—	—	—	—	11.2	221	210	0.293
.. 27	S	18.30	1018	315	199	145	107	—	221	222	—	12.0	199	215	0.287
July 18	K	11.49	1006	313	199	147	109	—	225	229	—	11.6	213	221	0.263
Aug. 14	S	7.50	1026	319	203	150	111	82	225	225	225	10.8	244	223	0.252
.. 14	S	13.3	1026	320	203	150	110	81	221	222	224	10.7	248	222	0.252
.. 15	S	7.55	1027	325	207	150	110	80	221	219	215	12.5	190	211	0.254
.. 15	K	18.00	1027	322	205	149	109	79	216	217	219	12.9	177	209	0.254
.. 16	K	7.00	1025	322	205	149	109	80	216	220	222	13.0	176	210	0.246
.. 17	S	8.00	1019	321	206	152	113	83	225	227	231	12.1	204	221	0.249
.. 19	K	7.10	1012	311	198	147	—	—	230	—	—	10.4	253	223	—
.. 20	S	8.00	1011	309	196	145	107	79	227	225	226	10.3	254	221	—
.. 22	K	7.00	1001	301	193	143	—	—	228	—	—	8.5	327	229	0.283
Sept. 17	S	7.55	1013	308	194	143	105	—	221	221	—	10.9	229	217	0.236

Places of ascent: S = Sealand (Chester), K = Kew.

It is at once evident that there is a close connection between the amount of ozone and the pressure in the upper air. A diagram for the pressure at 9 km. is very similar to that for 12 km., and the connection is as well marked up to 16 km., above which there are very few results.

There is, of course, an annual variation in the various characteristics of the upper atmosphere, and, as has been shown above, there appears to be a marked annual variation in the amount of ozone. If these annual variations are eliminated, the range of pressure variation is reduced to about two-thirds of its former value, though it happens that the range of ozone values is not much affected. Fig. 6 (b) shows the connection between upper air data and ozone values when both annual variations have been eliminated by using the differences from monthly means ( $P_5$  has no annual variation).

We have estimated that the standard error of the mean ozone value found for any day is about 0.005 cm., and Mr. L. H. G. Dines informs us that the standard error of measurements of pressure at, say, 10 km. is about 1.5 mb. Making an estimate of the standard error involved in measuring the ozone and

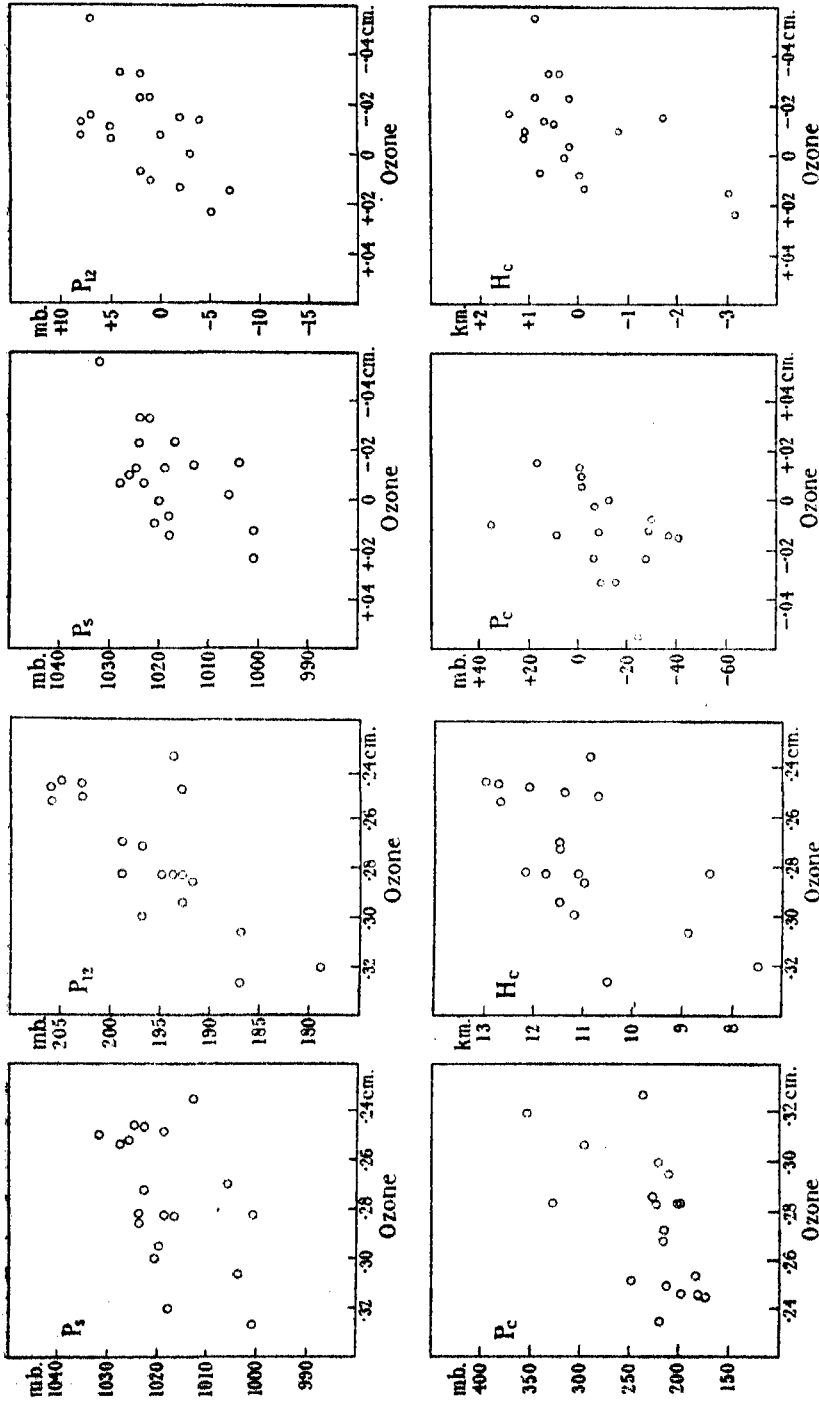


Fig. 6 (a).—Annual Variations not eliminated.

Fig. 6 (b).—Annual Variations eliminated.

pressures at different times and places, we can obtain an estimate of the total standard error of the upper air data. Using these values, we may correct the observed correlation coefficients for the known errors of observation by the ordinary statistical formula.

The following Table VIII gives the observed correlation coefficients both with and without eliminating the annual variations, and also the values corrected for observational error, as explained above.

Table VIII.

	Correlation coefficients.				Assumed errors of observation.
	Uncorrected for errors.		Corrected for errors of observation.		
	Incl. ann. variation.	Ann. var. eliminated.	Incl. ann. variation.	Ann. var. eliminated.	
P <sub>1</sub> .....	- 0.50 ± 0.12	- 0.56 ± 0.11	—	—	—
P <sub>2</sub> .....	- 0.71 ± 0.08	- 0.66 ± 0.09	- 0.75	- 0.73	2½ mb.
P <sub>12</sub> .....	- 0.78 ± 0.06	- 0.53 ± 0.11	- 0.83	- 0.81	2 mb.
P <sub>c</sub> .....	+ 0.59 ± 0.10	+ 0.52 ± 0.11	+ 0.60	+ 0.53	4 mb.
H <sub>c</sub> .....	- 0.62 ± 0.09	- 0.52 ± 0.11	- 0.62	- 0.52	0.2 km.
T <sub>c</sub> .....	+ 0.28 ± 0.14	+ 0.49 ± 0.12	+ 0.29	+ 0.51	1.0° C.

It would be unwise to place too much reliance on results based on only 19 observations, but the corrected correlation coefficients are remarkably high. The two days, March 17 and September 17, lower the correlation coefficient enormously, the uncorrected value for  $P_{12}$  rising to 0.88 if these days are omitted.

§ 7 (f) *Connection with Number of Sunspots.*—Whether the ozone is formed in the extreme upper atmosphere by ultra-violet radiation from the sun, or by electrical discharges in auroræ, it is not unlikely that some connection would be shown between the amount of ozone and solar activity. We have taken the provisional sunspot numbers published by Wolfer in the 'Meteorologische Zeitschrift,' for comparison with ozone values. Dividing the days in each month into three classes of high, medium and low sunspot numbers, the mean value of the ozone on days associated with many sunspots is 0.275 cm., and that for few sunspots is 0.298 cm. Thus high sunspot numbers seem to be associated with low ozone values. A similar tendency is seen if the ozone values and sunspot numbers are plotted on a dot diagram; connection is not very

close, but this could not be expected in view of the large barometric pressure effect.

Humphries\* has suggested that the lower average temperature of many parts of the earth at times of sunspot maximum may be explained by smaller amounts of ozone in the upper air, owing to the ultra-violet light being reduced by scattering in the corona, which is more extensive at times of sunspot maximum. The sign of the variation found here agrees with his theory, but the theory seems to have two serious objections: (1) if the corona absorbs and scatters a large amount of light, it should appear brighter than seems to be the case, though photographs in the extreme ultra-violet would be of interest; (2) there is definite evidence of greater rainfall at times of sunspot maximum, and, since the sign of the temperature correlation is positive in extremely dry localities, it may well be that the greater cloudiness and rainfall produce the lower temperature.

Dr. Chree† has shown that the ozone appears to be connected with terrestrial magnetic conditions, days with large values of ozone being associated with days of high magnetic character. From this one would expect days with many sunspots to be associated with days of much ozone. It may, therefore, be well to regard the existence of a relation between ozone and sunspots as still uncertain, and the possibility of the errors discussed above in § 5 (b) (iv) must be kept in mind.

§ 7 (g) *Connection with Solar Constant*.—Dr. Abbott has kindly supplied us with provisional solar constant values, but a preliminary examination does not indicate any close connection with the ozone values.

§ 7 (h) *Formation and Height of the Ozone*.—The only agencies likely to produce ozone in large quantities in the atmosphere are (i) ultra-violet light from the sun, (ii) electrical discharges in the aurora, (iii) electric discharges in thunderstorms. The observations of Rayleigh and Götz show that there is very little ozone in the lower atmosphere, and, indeed, one would hardly expect that much ozone could exist in the troposphere in the presence of atmospheric dust, some of which is oxidisable and all of which affords a large surface on which the ozone will decompose into oxygen, so that the ozone can hardly be formed by thunderstorms.

If the ozone be formed in the aurora it will probably be formed at heights above 100 km., while if it is formed by the wave-lengths of the sun's ultra-violet radiation which are absorbed by oxygen, it must be formed at heights

\* 'Physics of the Air.'

† See an adjacent paper.

above 40 km. Recent observations by Cabannes and Dufay\* give an effective height of 50 km., but the close connection with the pressure at about 10 km. indicates that a considerable portion must be at a much lower level, for there is good evidence that the pressure changes due to cyclones and anticyclones do not extend above about 20 km. It has been shown that oxygen is transformed into ozone by wave-lengths in the oxygen absorption band ( $<1800 \text{ \AA}$ ), and that ozone is decomposed again by (at least some of) the wave-lengths which it absorbs.

If the ozone be formed by the action of ultra-violet light, there will probably be a region at about 40 to 50 km. where the concentration of ozone will be governed by the equilibrium between the rate of formation by the shorter wave-lengths and the rate of decomposition by the longer wave-lengths. From this level it will probably sink down owing to its high molecular weight.

§ 7 (i) *Cause of the Connection between Atmospheric Pressure and Ozone.*—In the present limited state of our knowledge, it is not very profitable to speculate on this subject. Prof. Lindemann pointed out some time ago that the presence of ozone must raise the radiation equilibrium temperature of the earth's atmosphere, and that if the amount of ozone varied, the resulting temperature changes would cause variations in the pressure of the air below them. Again, if the ozone be formed at great heights and slowly sinks through the stratosphere, until it comes into the troposphere, where it is decomposed by dust, etc., then the greater the amount of air in the stratosphere, the greater will be the amount of ozone. Against this view is the fact that the correlation is closer with pressure at any fixed height than with either the height of the tropopause or the pressure at this level. Again, it is not unlikely that the origin of the air current has a large effect. When more observations are available, we shall be able to test such hypotheses with greater certainty.

In the meantime, in view of the interest of the pressure-ozone relation, arrangements are being pushed forward for making simultaneous daily measurements of the ozone at six widely distributed stations in N.W. Europe during 1926. From these measurements it should be possible to determine the distribution of ozone round various types of pressure distribution. By the kindness of the Smithsonian Institution measurements are also to be made at Montezuma, Chili, which will give an indication of the variation of ozone in tropical regions, and at a place where weather conditions are almost invariable. Thus real or apparent changes (*cf.* § 5 (b) (iv) ) in the amount of ozone, due to

\* 'Comptes Rendus,' August, 1925.

changes in the sun, should be separated from those due to local pressure variations.

In conclusion we wish to express our thanks to Prof. F. A. Lindemann, F.R.S., for the help he has afforded us throughout the whole of this work, and the many valuable criticisms and suggestions which he has given. The work was made possible by a grant to one of us from the Department of Scientific and Industrial Research, which we desire gratefully to acknowledge.

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*Atmospheric Ozone and Terrestrial Magnetism.*

By C. CHREE. Sc.D., LL.D., F.R.S.

(Received December 29, 1925.)

It is now generally believed that magnetic disturbance is primarily due to the special development or modification of electrical currents in the upper atmosphere. During magnetic disturbance the regular diurnal variation is enhanced, which suggests a general increase of electrical conductivity. It is not a far step to suppose that a decided change of electrical conditions in the upper atmosphere may be associated with some change at lower levels. In a presidential address\* to the Royal Meteorological Society I made the suggestion that something might result from a comparison of meteorological or electrical phenomena on days of high and low magnetic disturbance. The idea so far recommended itself to the meteorologists on the National Committee of Geodesy and Geophysics as to lead them to propose at the meeting of the International Union held in October 1924, at Madrid, that international funds should be applied to an investigation on these lines. This suggestion was not, however, approved.

On seeing the data contained in a preliminary account of the earlier of the ozone observations now discussed by Messrs. D. N. Harrison and G. M. B. Dobson, which was given to the Royal Meteorological Society, it occurred to me that they afforded suitable material for the kind of comparison I had suggested. On mentioning this to Dr. Dobson, he sent me the data obtained up to June 14.

For the investigation contemplated the most suitable magnetic data would have been the international magnetic character figures assigned at De Bilt.

\* 'Quarterly Journal Roy. Met. Soc.,' vol. 50, p. 96.



Each day receives a character figure varying from 0·0 (very quiet) to 2·0 (very disturbed). These international figures, however, are not issued until some considerable time after the year's end. The only magnetic data immediately available were the character figures on the scale 0 (quiet), 1 (moderately disturbed), 2 (highly disturbed), which appear on the weekly sheets of magnetic declination now issued by the Astronomer Royal for the benefit of mining engineers. The magnetic information thus supplied is comparatively rough, but experience has shown that character figures from a single station, when carefully assigned, make not a bad substitute for the international figures for the purposes of a preliminary enquiry.

The results obtained with the earlier ozone figures suggested a closer relation with the magnetic character than was expected, but it was clearly desirable to await further data. The investigation was resumed on the receipt from Dr. Dobson of the ozone figures obtained up to November, 1925. As the results from the later months supported those from the earlier months, it seems well to publish them, with the details necessary to enable the reader to form an independent judgment.

No fine distinctions of magnetic character being possible, the ozone observations were arranged in three groups, according as the Greenwich character figure on the day of observation was 0, 1 or 2. On the few occasions when two ozone observations had been taken on the same day, the arithmetic mean of the observed values was accepted. The mean ozone figures for each group of days in each month appear in Table I, the number of days available in each case being given in brackets. There were two months in which character 2 had been assigned to no day for which ozone figures existed, and three months in which it had been assigned to only one such day. In view of this, results are given in Table I for a group which includes both character 1 and character 2 days.

As the mean ozone figure varies a good deal for different months, it was decided to include in Table I two sets of mean values, the first, A, allowing equal weight to each month, the second, B, equal weight to each day. The mean ozone figure for character 2 days, being dependent on only eight months, is not altogether comparable with the other means. The final means arrived at in the two ways associate a higher ozone value with increased magnetic disturbance. Confining our attention to the first and last columns of Table I, it will be seen that the monthly differences are not all in one direction. In one month the figures in the two columns are identical, and in two months the figure in the last column is the smaller. But the differences in these two months are small,

while there is only one of the seven months where the figure in the last column is the larger in which the difference is not fairly substantial.

One of the features obvious in the ozone figures was a tendency to runs of high and low values. This is also a property of magnetic character figures, though in years like 1925 long runs are more common for quiet than for disturbed conditions. Thus, even if we accepted the final means in Table I as freed from accidental features, we should not be entitled to assume that high ozone and large magnetic disturbance are synchronous. The one event might follow the other after a day or more. Table II shows the results of a not altogether successful attempt to investigate the matter further. It utilises all the days of ozone observation which were immediately preceded and succeeded by days for which ozone results also existed. Calling any such day  $n$ , this implies the existence of ozone data for the three successive days  $n - 1$ ,  $n$  and  $n + 1$ . The days  $n$  were divided into two groups, one including all days of magnetic character 0, the other all days of character 1 or 2. Mean ozone figures were calculated for either group of  $n$  days and the associated groups of  $n - 1$  and  $n + 1$  days. The results are given in Table II, along with the number of  $n$  days available in each month. Two sets of final means are given, as in Table I, the first, A, assigning equal weight to each month, the second, B, to each day. In view of the small number of days available, the second means in this case are probably the best.

The differences between the mean results in columns  $n - 1$ ,  $n$  and  $n + 1$  of the same group are too small to justify a final decision, but the evidence, so far as it goes, suggests that the difference between the two groups is greater for the  $n - 1$  than the  $n + 1$  days, and is pretty much the same for the  $n - 1$  and the  $n$  days. What this suggests is that the day of much ozone rather precedes than follows the day of high magnetic character.

To carry the investigation further calls not merely for more days, but for sequences of more than three days. Thus some other mode of attack had to be devised. The simplest plan was obviously to group the days not according to magnetic character, but according to the ozone figure. As magnetic characters exist for all days, we can in this way utilise practically all the days for which ozone figures exist. Supposing the number of these days in any one month to be  $2i$  or  $2i + 1$ , the  $i$  days of largest ozone figure formed the one group, the  $i$  days of lowest ozone figure the other. Of 23 days available in September, 12 had to be assigned to the group of high ozone days, because two days with equal ozone figures were eligible for the last place. Originally the investigation was confined to the 5-day sequence  $n - 2$  to  $n + 2$ , but it

was found expedient to extend it to the 11-day sequence  $n - 5$  to  $n + 5$ . The results appear in Table III. The figures tabulated are the mean Greenwich characters for the two groups of  $n$  days and their associated days. As before, two sets of final mean values are given. The first, A, assigns equal weight to each of the ten months, the second, B, equal weight to each of the 95 (or 96) days.

With so rough a measure of magnetic disturbance, smoothness cannot be expected in the sequence of figures in individual months, and there is obviously a large "accidental" element in any one month. But the final means, whether A or B, especially those for the days associated with the days of most ozone, are comparatively smooth. The mean character figure for the 191 days used was 0.64. The departure from that figure shown by the means for the columns  $n - 2$  to  $n + 2$  in the group of high ozone days, and the means for the columns  $n - 1$  to  $n + 3$  associated with the low ozone days, can hardly be ascribed to accident. In the case of columns  $n + 1$  the excess in the final mean character figure, whether A or B, for the days associated with the high ozone days over the days associated with the low ozone days is 0.36, or 56 per cent. of the all-day mean character figure 0.64. The fact that the excess is decidedly greater for column  $n + 1$  than for column  $n - 1$  in Table III suggests, exactly as in the case of Table II, that the day of high ozone is rather the precursor than the follower of the day of high magnetic character.

This is hardly what we should expect *a priori*, since any influence coming from without would naturally show itself earlier in the upper than in the lower atmosphere. The ordinary magnetic storm, however, centres in the late evening G.M.T., and extends to two Greenwich days. The observed phenomenon might signify that the first of these tends to have a higher ozone figure than the second.

Table IV is intended to show more exactly how the difference between the two groups of days in Table III comes about. It gives the number of days of magnetic characters 0, 1, and 2 for columns  $n - 2$  to  $n + 2$  in both groups. To get an identical number of days, 95, for each group, one of the two September days referred to above was omitted. The day retained was the one least favourable to a difference between days of high and low ozone. If we take the whole five columns in Table IV, we find that the number of days of character 2 associated with the group of days of higher ozone is exactly double the number associated with the group of days of lower ozone. In the case of column  $n + 1$  the ratio is as 3 to 1.

Table V gives the results of an attempt to see whether the ozone figures show the 27-day interval (solar rotation period) usually exhibited by magnetic

character figures. In this case the two contrasted groups of days  $n$  were intended to be composed—the one of the five days of most ozone of the month, the other of the five days of least ozone. But ozone information was lacking for the days from 26 to 28 days subsequent to a good many of the days that would naturally have been selected. All the November days had to be omitted for this reason. In fact, to get at all an adequate number, days had to be included which did not contribute to all the columns  $n + 26$  to  $n + 28$ . Thus the monthly means in these columns are in some cases derived from a varying number of days. In this kind of investigation accident plays a very large part in the results from a single month, even in the case of magnetic character figures free from gaps. In the present case the monthly figures are given only to make a full disclosure of the uncertainties involved. The differences between the two sets of final means for columns  $n + 27$  and  $n + 28$ , viz., 0·010 cm. and 0·013 cm., form as high a percentage of the primary pulse (*i.e.*, the difference 0·043 cm., between the means in columns  $n$ ) as is usual in the case of magnetic character figures. But perhaps all we are justified in saying is that the results are not unfavourable to the existence of the 27-day interval. This is more than could be said in the case of the published values of the “solar constant.”\*

It is never prudent to accept the results of a single year as final. Events analogous to the breaking of the bank at Monte Carlo do occur occasionally, even in Nature. But it seems abundantly clear that the systematic continuation of ozone observations for some time to come is desirable in the interests of terrestrial magnetism.

Table I.—Ozone on Days of Different Magnetic Character.

Month.	Character.			
	0	1	2	1 or 2
	cm.	cm.	cm.	cm.
February .....	0·328 (4)	0·322 (3)	—	0·322 (3)
March .....	0·281 (9)	0·294 (5)	0·330 (1)	0·300 (6)
April .....	0·311 (8)	0·327 (15)	0·337 (1)	0·328 (16)
May .....	0·292 (14)	0·309 (11)	0·300 (5)	0·306 (16)
June .....	0·281 (10)	0·276 (14)	0·284 (4)	0·278 (18)
July .....	0·273 (8)	0·273 (6)	—	0·273 (6)
August .....	0·250 (12)	0·267 (5)	0·278 (3)	0·271 (8)
September .....	0·251 (12)	0·253 (7)	0·250 (4)	0·252 (11)
October .....	0·216 (8)	0·228 (4)	0·232 (6)	0·230 (10)
November .....	0·216 (9)	0·246 (5)	0·264 (1)	0·249 (6)
Mean A .....	0·270	0·279	0·284	0·281
„ B .....	0·267 (94)	—	—	0·283 (100)

\* ‘Roy. Soc. Proc.,’ A, vol. 109, p. 1.

Table II.—Ozone on Three Successive Days.

Month.	Character 0.				Character 1 or 2.			
	Days.	$n - 1$	$n$	$n + 1$	Days.	$n - 1$	$n$	$n + 1$
		cm.	cm.	cm.		cm.	cm.	cm.
February .....	1	0.318	0.305	0.365	1	0.335	0.307	0.294
March .....	3	0.284	0.271	0.293	5	0.309	0.301	0.287
April .....	6	0.307	0.317	0.329	10	0.334	0.336	0.331
May .....	13	0.291	0.292	0.292	15	0.307	0.307	0.302
June .....	10	0.275	0.281	0.278	14	0.283	0.276	0.279
July .....	5	0.273	0.270	0.268	6	0.272	0.273	0.271
August .....	6	0.248	0.247	0.250	4	0.264	0.270	0.260
September .....	7	0.258	0.258	0.252	7	0.257	0.251	0.253
November .....	4	0.229	0.209	0.203	3	0.240	0.256	0.248
Mean A .....	—	0.274	0.279	0.281	—	0.289	0.286	0.281
.. B .....	55	0.274	0.276	0.277	65	0.292	0.291	0.287

Table IV.—Number of Occurrences of Magnetic Characters 0, 1, 2 in Different Columns.

Column.	$n - 2$			$n - 1$			$n$			$n + 1$			$n + 2$		
Character.	0	1	2	0	1	2	0	1	2	0	1	2	0	1	2
Days of least ozone .....	49	38	8	53	33	9	56	31	8	56	33	6	57	29	9
Days of most ozone .....	38	42	15	35	44	16	36	42	17	34	43	18	38	43	14

Table V.—Ozone Data : 27-Day Interval.

Month.	Days of least ozone.				Days of most ozone.			
	$n$	$n + 26$	$n + 27$	$n + 28$	$n$	$n + 26$	$n + 27$	$n + 28$
	cm.	cm.	cm.	cm.	cm.	cm.	cm.	cm.
March .....	0.258	0.321	0.316	0.311	0.320	0.313	0.322	0.345
April .....	0.288	0.281	0.277	0.283	0.350	0.305	0.314	0.318
May .....	0.272	0.277	0.264	0.263	0.333	0.299	0.294	0.266
June .....	0.260	0.274	0.280	0.281	0.294	0.277	0.275	0.279
July .....	0.262	0.265	0.264	0.253	0.276	0.278	0.273	0.270
August .....	0.237	0.255	0.245	0.244	0.281	0.251	0.258	0.266
September .....	0.231	0.243	0.235	0.234	0.271	0.199	0.212	0.233
October .....	0.201	0.224	0.225	0.226	0.229	0.223	0.233	0.226
Mean .....	0.251	0.267	0.263	0.262	0.294	0.268	0.273	0.275
Excess for days of most ozone .....	—	—	—	—	0.043	0.001	0.010	0.013

Table III.—Magnetic Character on Days of Least and Most Ozone and Associated Days.

Month.	Days of least ozone and associated days.											Days of most ozone and associated days.										
	n-5	n-4	n-3	n-2	n-1	n	n+1	n+2	n+3	n+4	n+5	n-5	n-4	n-3	n-2	n-1	n	n+1	n+2	n+3	n+4	n+5
February	0.33	0.33	1.00	0.67	0.33	0.67	0.33	0.33	0.33	0.33	0.67	0.33	0.33	0.67	0.33	0.33	0.33	1.00	0.67	0.00	0.00	0.33
March	0.43	0.43	0.71	0.86	0.43	0.14	0.43	0.57	0.57	0.71	0.86	0.43	0.43	0.43	0.57	0.43	0.71	1.00	0.86	0.43	0.57	0.57
April	0.75	0.67	0.67	0.75	0.67	0.58	0.58	0.67	0.58	0.67	0.75	0.50	0.50	0.58	0.50	0.67	0.83	0.83	0.75	0.83	0.92	0.83
May	0.73	0.67	0.73	0.53	0.40	0.60	0.33	0.27	0.33	0.47	0.40	0.60	0.53	0.53	0.73	1.00	0.80	0.87	1.00	1.00	0.73	0.67
June	0.64	0.79	0.57	0.43	0.57	0.79	0.57	0.64	0.71	0.64	0.64	1.00	0.93	1.07	1.07	0.93	0.79	1.07	0.93	0.86	0.93	0.93
July	0.14	0.43	0.57	0.57	0.57	0.43	0.43	0.43	0.43	0.71	0.43	0.57	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.14	0.43	0.43
August	0.90	0.50	0.20	0.00	0.10	0.10	0.40	0.70	0.80	0.80	1.10	0.50	0.60	0.90	1.00	0.90	1.00	0.90	0.50	0.20	0.20	0.30
September	0.36	0.55	0.82	0.73	1.00	0.73	0.45	0.36	0.27	0.45	0.45	0.91	0.64	0.83	0.83	0.58	0.58	0.75	0.58	0.82	0.45	0.55
October	0.56	0.44	0.78	0.78	0.67	0.44	0.89	0.78	1.11	0.89	1.11	0.67	1.00	0.67	0.67	1.22	1.33	0.89	0.78	0.67	0.67	0.56
November	0.71	0.71	0.86	0.57	0.43	0.14	0.14	0.00	0.00	0.29	0.57	0.29	0.57	0.57	1.00	1.14	0.86	0.43	0.71	0.71	0.57	0.43
Mean A	0.56	0.53	0.69	0.59	0.52	0.46	0.46	0.48	0.51	0.60	0.70	0.58	0.60	0.65	0.75	0.76	0.77	0.82	0.72	0.60	0.52	0.56
" B	0.60	0.59	0.66	0.57	0.54	0.49	0.47	0.49	0.54	0.61	0.68	0.63	0.63	0.67	0.76	0.80	0.80	0.83	0.76	0.68	0.60	0.61
Mean Ozone—																						
A	—	—	—	—	—	0.258	—	—	—	—	—	—	—	—	—	—	0.293	—	—	—	—	—
B	—	—	—	—	—	0.259	—	—	—	—	—	—	—	—	—	—	0.292	—	—	—	—	—

*On a Set of Quartic Surfaces in Space of Four Dimensions ;  
and a Certain Involutory Transformation.*

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(Communicated by Prof. H. F. Baker, F.R.S.—Received November 5, 1925.)

There exists in space of four dimensions an interesting figure of 15 lines and 15 points, first considered by Stéphanos ('Compt. Rendus,' vol. 93, 1881), though suggested very clearly by Cremona's discussion of cubic surfaces in three-dimensional space. In connection with the figure of 15 lines there arises a quartic surface, the intersection of two quadrics, which is of importance as giving rise by projection to the Cyclides, as Segre has shown in detail ('Math. Ann.,' vol. 24, 1884). The symmetry of the figure suggests, however, the consideration of 15 such quartic surfaces; and it is natural to inquire as to the mutual relations of these surfaces, in particular as to their intersections.

In general, two surfaces in space of four dimensions meet in a finite number of points. It appears that in this case any two of these 15 surfaces have a curve in common; it is the purpose of the present note to determine the complete intersection of any two of these 15 surfaces. Similar results may be obtained for a system of cubic surfaces in three dimensions, corresponding to those here given for this system of quartic surfaces in four dimensions, since the surfaces have one point in common, which may be taken as the centre of a projection.

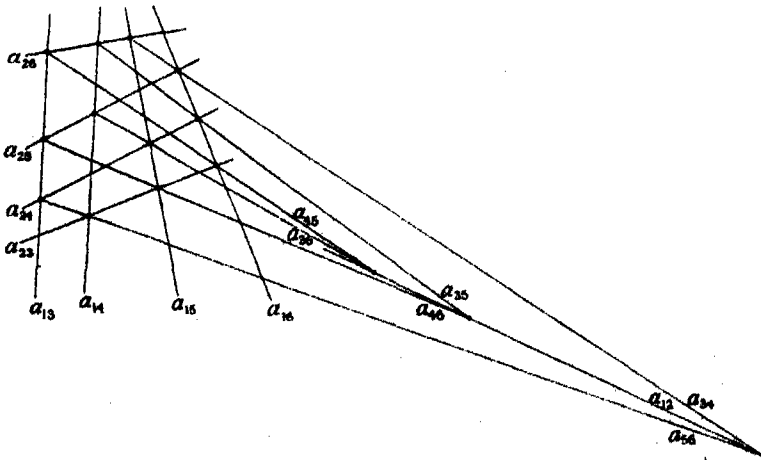


FIG. 1.

The properties of the configuration of 15 points and lines are most readily expressed by denoting the 15 lines by  $a_{rs}$  ( $r, s = 1, 2, 3, 4, 5, 6$ ), subject to  $a_{rs} \equiv a_{sr}$ , and such that two lines thereof intersect if, and only if, their duad numbers have no index in common. (See fig. 1.) Thus three lines pass through every point of the figure, while the points lie by threes upon the 15 lines. Moreover, the three skew lines  $a_{23}, a_{31}, a_{12}$ , for example, determine a threefold space, being all met by each of the lines  $a_{56}, a_{64}, a_{45}$ , which therefore lie in the space. One of the ten fundamental, or cardinal, spaces of the figure is thus defined, and may be denoted by  $a_{123(456)}$ , or briefly  $a_{123}$ . These spaces pass by fours through the lines of the figure:  $a_{123}, a_{124}, a_{125}, a_{126}$  through the line  $a_{12}$ . It is important to note that the remaining six-spaces may be taken in three pairs,  $a_{136}, a_{145}$ ;  $a_{146}, a_{135}$ ;  $a_{156}, a_{134}$ . The spaces  $a_{136}, a_{145}$  are then seen to contain the lines  $a_{36}, a_{45}$ , while these lines meet on the line  $a_{12}$ ; similarly, the spaces  $a_{146}, a_{135}$ , each contain the lines  $a_{46}, a_{35}$ ; and the spaces  $a_{156}, a_{134}$ , each contain the lines  $a_{56}, a_{34}$ . It will be seen later that this fact is put in evidence by the form of the equation to the surface.

The surface, constructed with reference to three skew lines and two fixed points, may be defined as the locus of the point of intersection of a plane drawn through any fixed point, K, to meet any three skew lines,  $a_{13}, a_{14}, a_{15}$ , with a plane drawn through another fixed point, K', to meet the same three lines, provided that the line KK' is skew to each of the lines  $a_{13}, a_{14}, a_{15}$ . The line KK' may then be denoted by  $a_{12}$ . It is, however, a property of the space of four dimensions that all planes meeting any four skew lines of which no three lie in a threefold space, meet also a further line: in other words, the planes meeting  $a_{13}, a_{13}, a_{14}, a_{15}$ , meet a line which may be denoted by  $a_{12}$ ; of such planes two may be drawn to pass through any point, O, of general position. Thus, given the system of 15 lines and a fixed point, O, we may take the points K, K' to be those in which the two planes, through O and meeting  $a_{13}, a_{14}, a_{15}, a_{16}$ , meet the line  $a_{12}$ . Moreover, the planes which meet the lines  $a_{23}, a_{24}, a_{25}, a_{26}$ , meet the line  $a_{12}$ ; of these planes, those which pass through O meet  $a_{12}$  in the same two points as do those which meet  $a_{13}, a_{14}, a_{15}, a_{16}$ . In fact, the quartic surface defined with these two points and the lines  $a_{23}, a_{24}, a_{25}$ , coincides with that defined above with the same two points and the lines  $a_{13}, a_{14}, a_{15}$ . Thus there is one quartic surface, when the system of 15 lines and the point O are given, defined with reference to the line  $a_{12}$ . It may be denoted by  $\Gamma(a_{12})$ . Similarly, one quartic surface may be defined uniquely with reference to any other line of the figure, and 15 quartic surfaces



are thus suggested, all passing through  $O$ , one corresponding to each line of the figure.

Any one of these surfaces is the intersection of two quadrics which define a pencil of quadrics containing the surface. There are five quadric cones belonging to the pencil, and their vertices form a self-polar pentad for the surface: the polar space of any vertex of the pentad, with respect to any quadric of the pencil, being the space defined by the other four vertices of the pentad. The self-polar pentad for the surface  $\Gamma(a_{12})$  has  $K, K'$ , on the line  $a_{12}$ , as two vertices, together with vertices  $U, V, W$ , obtained by taking the six cardinal spaces which do not contain the line  $a_{12}$ , and pairing them in the way already indicated. Then  $U$  is the point of intersection of the two pairs of spaces  $a_{135}, a_{146}$ ;  $a_{136}, a_{145}$ : that is, of the plane of the two lines  $a_{36}, a_{45}$  with the plane of the two lines  $a_{35}, a_{46}$ ; while  $V$  is given by the two pairs of spaces  $a_{135}, a_{146}$ ;  $a_{134}, a_{156}$ ;  $W$  is given by the pairs of spaces  $a_{134}, a_{156}$ ;  $a_{136}, a_{145}$ . Thus, if the points of intersection of the lines  $a_{34}, a_{56}$ ;  $a_{36}, a_{45}$ ;  $a_{35}, a_{46}$ , be denoted by  $L, M, N$ , respectively, the points  $U, V, W$ , may be considered as corresponding respectively to the points  $L, M, N$ , when the latter are regarded as points of the line  $a_{12}$ . It is now possible to show that only

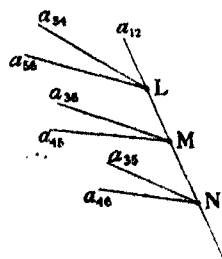


FIG. 2.

15 points, such as  $U, V, W$ , arise for the self-polar pentads of all the 15 quartic surfaces. The point  $L$ , for instance, lies also upon the lines  $a_{34}, a_{56}$ , and upon each of these lines lie two further points of the configuration. Consider the line  $a_{34}$ : it contains besides  $L$  the points of intersection of the lines  $a_{15}, a_{26}$ ; and  $a_{16}, a_{25}$ , respectively, while these pairs of lines lie in the spaces  $a_{135}, a_{145}$ ; and  $a_{136}, a_{146}$ , respectively. Thus the same spaces, grouped differently, are obtained whether  $L$  is regarded as a point of the line  $a_{12}$ , or of the line  $a_{34}$ , or of the line  $a_{56}$ . The point of intersection  $U$ , of the spaces, thus corresponds uniquely to the point  $L$ . Similarly, the points  $V, W$  may be considered as corresponding to the points  $M, N$  of the line  $a_{12}$ . It follows that there are only 15 points which are vertices of the self-polar pentads belonging to the 15 quartic surfaces, other than those vertices which lie by twos upon lines of the figure. It is remarkable that these 15 points do not depend upon the point  $O$ , by which the 15 surfaces are defined, but are determined by the fundamental configuration alone.

The equations of the surfaces are now taken into account for the determination of their intersections. Let  $P = 0, P' = 0$ ;  $Q = 0, Q' = 0$ ;  $R = 0$ ,

$R' = 0$ , denote respectively the spaces which contain the pairs of lines concurrent with the line  $a_{12}$ , namely,  $a_{156}, a_{134}; a_{146}, a_{135}; a_{145}, a_{136}$ ; and let  $p, p', q, q', r, r'$  be the respective values of  $P, P', Q, Q', R, R'$  at the point  $O$ . Then the equation of the surface  $\Gamma(a_{12})$ , associated with the line  $a_{12}$  is, in fact

$$\frac{PP'}{pp'} = \frac{QQ'}{qq'} = \frac{RR'}{rr'}.$$

Moreover, we may suppose  $P + Q + R + P' + Q' + R' = 0$ . The remaining four cardinal spaces,  $a_{124}, a_{125}, a_{126}, a_{123}$  may be denoted by  $X, Y, Z, T$ , respectively; these all pass through the line  $a_{12}$ . It is then found that the space  $T$  is given by the equation  $P + Q + R = 0$ ; it passes through the line  $a_{23}$ , which is common to the spaces  $P, Q, R$ ; and it is found that the equations of the spaces  $X, Y, Z$  are  $P' + Q + R = 0, P + Q' + R = 0, P + Q + R' = 0$ , respectively.

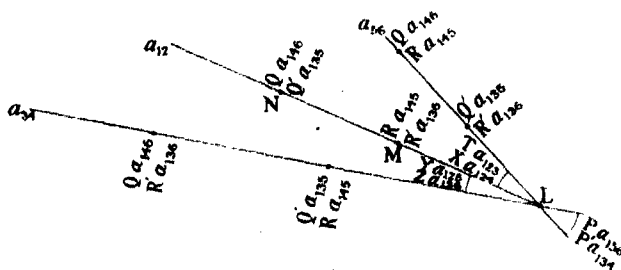


FIG. 3.

The accompanying diagram indicates the arrangement of the spaces already explained; it consists of the three lines  $a_{12}, a_{34}, a_{56}$ , meeting in the point  $L$ , together with the pairs of further points which lie upon these lines, while the spaces indicated at any one of these points are those which contain the other two lines of the figure which pass through that point: From the equation of the surface associated with the line  $a_{12}$  the equation of any other of the 15 surfaces may then be written down.

Any three cardinal spaces, one from each of the three pairs which define the surface, meet in a line which is one of the original 15. From the index notation for these spaces it is easily seen that the eight lines so found, lying upon the surface  $\Gamma(a_{12})$ , whose equation is

$$\frac{PP'}{pp'} = \frac{QQ'}{qq'} = \frac{RR'}{rr'},$$

namely,

$$\begin{aligned} P' = Q' = R' = 0, \quad P' = Q = R = 0, \quad P = Q' = R = 0, \quad P = Q = R' = 0, \\ P = Q = R = 0, \quad P = Q' = R' = 0, \quad P' = Q = R' = 0, \quad P' = Q' = R = 0. \end{aligned}$$

are respectively the lines  $a_{13}, a_{14}, a_{15}, a_{16}, a_{23}, a_{24}, a_{25}, a_{26}$ ; these are the eight lines of the configuration which do not meet the line  $a_{12}$ , with which the surface is associated. The surface contains eight other lines, which do not belong to the original configuration; they are obtainable, from the eight already found, by harmonic inversion in either one of the spaces of the self-polar pentad which are opposite to the vertices  $K, K'$ ; or may be determined as follows: let the transversal from  $K$  to the lines  $a_{13}, a_{23}$  meet these lines in  $I, J$ , and let the transversal from  $K'$  to the lines  $a_{13}, a_{23}$  meet these lines in  $I', J'$ . The lines  $IJ', I'J$  lie upon the surface  $\Gamma(a_{12})$ . The remaining lines of the surface are obtained similarly when  $a_{14}, a_{24}$ ;  $a_{15}, a_{25}$ ;  $a_{16}, a_{26}$  are taken instead of  $a_{13}, a_{23}$ . Thus, of the 16 lines upon any one of the surfaces, the set of eight which does not belong to the fundamental configuration is distinct from that obtained for any other of the 15 surfaces, and hence can form no part of the intersection of any two of the surfaces.

The intersection of two of the surfaces may be that of:

- (1) Any two surfaces associated with two intersecting lines of the configuration,
- (2) Any two surfaces associated with two non-intersecting lines of the configuration.

For the first case consider, for example, any two of the three surfaces associated with the lines  $a_{12}, a_{34}, a_{56}$ , concurrent in the point  $L$ . Of the eight lines of the figure which do not meet  $a_{12}$  and which, therefore, lie on the surface  $\Gamma(a_{12})$ , four meet the line  $a_{34}$  and do not meet the line  $a_{56}$ , while the other four meet the line  $a_{56}$  and do not meet the line  $a_{34}$ . Thus any two of these surfaces have four lines in common, forming two pairs of intersecting lines; for the surfaces  $\Gamma(a_{12}), \Gamma(a_{34})$ , the lines are  $a_{13}, a_{14}, a_{23}, a_{24}$ .

It can now be shown that these surfaces  $\Gamma(a_{12}), \Gamma(a_{34})$  have a conic in common; and no further common points, other than those lying upon the lines  $a_{13}, a_{14}, a_{23}, a_{24}$ , together with the point  $O$ . The equations to the surfaces being

$$\frac{PP'}{pp'} = \frac{QQ'}{qq'} = \frac{RR'}{rr'},$$

$$\frac{XT}{xt} = \frac{QR'}{qr'} = \frac{Q'R}{q'r'},$$

where

$$X = P' + Q + R, T = P + Q + R, x = p' + q + r, t = p + q + r,$$

their self-polar pentads have a vertex,  $Q = Q' = R = R' = 0$ , in common. The space  $Q/q = R/r$  meets  $\Gamma(a_{12})$  in a quartic curve which is the intersection

of two quadrics in threefold space; this curve contains as part of itself the two lines  $P = Q = R = 0$  and  $P' = Q = R = 0$ ; the remaining part is thus a conic,  $\sigma$ , which therefore meets these two lines. Similarly, the space  $Q'/q' = R'/r'$  meets  $\Gamma(a_{12})$  in a quartic curve consisting of the lines  $P = Q' = R' = 0$ , and  $P' = Q' = R' = 0$ , together with a conic,  $\sigma'$ . But the plane common to the spaces  $Q/q = R/r$ ,  $Q'/q' = R'/r'$ , passes through the vertex  $Q = Q' = R = R' = 0$  of the self-polar pentad, and lies on the quadric cone with this vertex, containing the surface; it thus meets  $\Gamma(a_{12})$  in a conic. Hence  $\sigma$  and  $\sigma'$  are the same conic, which thus meets the four common lines of the two surfaces. Similarly, this common plane of the spaces  $Q/q = R/r$ ,  $Q'/q' = R'/r'$  meets  $\Gamma(a_{34})$  in a conic meeting the four lines common to the two surfaces and passing through  $O$ . This conic is then common to the two surfaces. There are no further common points of  $\Gamma(a_{12})$ ,  $\Gamma(a_{34})$ ; for the common points for which  $Q' = 0$  or  $R' = 0$  lie upon one of the four lines, while if  $Q'$ ,  $R'$  are neither zero, the equations

$$\frac{QQ'}{qq'} = \frac{RR'}{rr'}, \quad \frac{QR'}{qr'} = \frac{Q'R}{q'r'},$$

give

$$\frac{Q^2}{q^2} = \frac{R^2}{r^2},$$

of which  $Q/q = R/r$  has been considered.

If, then,

$$\frac{Q}{q} = -\frac{R}{r},$$

we must have

$$\frac{Q'}{q'} = -\frac{R'}{r'}.$$

Put

$$Q = \lambda q, \quad R = -\lambda r, \quad Q' = -\mu q', \quad R' = \mu r'.$$

Then for common points of  $\Gamma(a_{12})$ ,  $\Gamma(a_{34})$ ,

$$\frac{PP'}{pp'} = -\lambda\mu, \quad \frac{XT}{xt} = \lambda\mu;$$

or

$$\left. \begin{aligned} P(Q' + R' + P + Q + R) - \lambda\mu pp' &= 0 \\ (P + Q' + R')(P + Q + R) + \lambda\mu xt &= 0 \end{aligned} \right\},$$

or

$$\left. \begin{aligned} P^2 + P(Q + R + Q' + R') - \lambda\mu pp' &= 0 \\ P^2 + P(Q + R + Q' + R') + (Q + R)(Q' + R') + \lambda\mu xt &= 0 \end{aligned} \right\},$$

Hence

$$-\lambda\mu(q - r)(q' - r') + \lambda\mu xt + \lambda\mu pp' = 0.$$

Thus, unless  $\lambda$  or  $\mu$  is zero (in which case  $Q = R = 0$ , or  $Q' = R' = 0$ , or both, which leads to the common lines already considered), we must have

$$(q - r)(q' - r') + (p + q + r)(p + q' + r') + p(p + q + r + q' + r') = 0,$$

which gives

$$2p^2 + 2p(q + r + q' + r') + 2qq' + 2rr' = 0,$$

and this necessitates

$$-pp' + qq' + rr' = 0,$$

and this is not true for a general position of the point O.

*It has thus been shown that two of the 15 quartic surfaces associated with two intersecting lines of the fundamental configuration have in common a conic passing through the given common point O of the surfaces, together with two pairs of intersecting lines, which are the lines of the original figure not meeting the two lines with which the surfaces are associated. These four lines all meet the common conic.*

For the case of two surfaces associated with two skew lines, the surfaces  $\Gamma(a_{12})$ ,  $\Gamma(a_{13})$  give a typical example. The equations to these two surfaces are

$$\frac{PP'}{pp'} = \frac{QQ'}{qq'} = \frac{RR'}{rr'} \quad (i)$$

and

$$\frac{P(P' + Q + R)}{p(p' + q + r)} = \frac{Q(Q' + R + P)}{q(q' + r + p)} = \frac{R(R' + P + Q)}{r(r' + p + q)} \quad (ii)$$

The surfaces are seen to have four lines in common,  $P = Q = R = 0$ ,  $P' = Q = R = 0$ ,  $Q' = R = P = 0$ ,  $R' = P = Q = 0$ , which are the three lines  $a_{14}$ ,  $a_{15}$ ,  $a_{16}$ , and their transversal  $a_{23}$ ; these are the four lines of the fundamental configuration which do not meet  $a_{12}$  or  $a_{13}$ . The surfaces will be shown to have one point in common besides the point O, and no further points other than those which lie upon the lines  $a_{14}$ ,  $a_{15}$ ,  $a_{16}$ ,  $a_{23}$ . For consider the various possibilities:  $Q = R = 0$  involves  $P = 0$  or  $P' = 0$ , each of which gives one of the common lines; similarly  $R = P = 0$  requires  $QQ' = 0$ ,  $Q(Q' + R + P) = 0$ , so that  $R = P = Q' = 0$ ; also  $P = Q = 0$  requires  $RR' = 0$ ,  $R(R' + P + Q) = 0$ , so that  $P = Q = R' = 0$ , which in each case are lines common to the surfaces. Excluding these possibilities, we may eliminate  $P'$ ,  $Q'$ ,  $R'$  by means of the equations (i), (ii) and find, in the plane of  $P$ ,  $Q$ ,  $R$ , a quartic curve with double points at  $Q = R = 0$ ,  $R = P = 0$ ,  $P = Q = 0$ , together with a conic passing through these points. The quartic

curve and the conic intersect in two further points, which can be shown to lead to two common points for the surfaces  $\Gamma(a_{12})$ ,  $\Gamma(a_{13})$ , namely, the point  $(p, q, r, p', q', r')$  and the point derived from this by the involutory transformation of the space of four dimensions, which we now explain.

Let

$$x = 0, \quad y = 0, \quad z = 0, \quad x' = 0, \quad y' = 0, \quad z' = 0,$$

subject to

$$x + y + z + x' + y' + z' = 0,$$

be the equations of six threefold spaces. Put, for brevity,

$$a = -xx' + yy' + zz' + yz, \quad b = xx' - yy' + zz' + zx,$$

$$c = xx' + yy' - zz' + xy,$$

and take  $X, Y, Z, X', Y', Z'$ , so that

$$X = -bc, \quad Y = -ca, \quad Z = -ab, \quad X' = axx', \quad Y' = byy', \quad Z' = czz'.$$

It can then be shown that

$$X + Y + Z + X' + Y' + Z' = 0$$

and

$$x : y : z : x' : y' : z' = -BC : -CA : -AB : AXX' : BYY' : CZZ'$$

where

$$A = -XX' + YY' + ZZ' + YZ, \quad B = XX' - YY' + ZZ' + ZX,$$

$$C = XX' + YY' - ZZ' + XY.$$

In fact, the equations give

$$X' + Y + Z = -ax(x' + y + z), \quad X + Y' + Z' = ax(x' + y + z)$$

and similar results, together with

$$A = abcyz, \quad B = abczx, \quad C = abcxz,$$

from which the statements made follow at once.

Each of the surfaces  $\Gamma(a_{12})$ ,  $\Gamma(a_{13})$  is then transformed into itself by this involution. In particular, since the surfaces have the common point  $(p, q, r, p', q', r')$ , they also have the common point  $(P, Q, R, P', Q', R')$ , which is derived from  $(p, q, r, p', q', r')$  by the equations by which  $(X, Y, Z, X', Y', Z')$  is obtained from  $(x, y, z, x', y', z')$ .

This transformation may, however, be considered as the combination of

two involutory transformations relating to space of five dimensions. One of these two involutory transformations is expressed by

$$\xi = yz, \quad \eta = zx, \quad \zeta = xy, \quad \xi' = xx', \quad \eta' = yy', \quad \zeta' = zz', \quad (\text{A})$$

which leads to

$$x : y : z : x' : y' : z' = \eta\zeta : \zeta\xi : \xi\eta : \xi\xi' : \eta\eta' : \zeta\zeta'$$

and transforms the fourfold space  $x + y + z + x' + y' + z' = 0$  into the quadric

$$\eta\zeta + \zeta\xi + \xi\eta + \xi\xi' + \eta\eta' + \zeta\zeta' = 0. \quad (\text{iii})$$

The other involutory transformation is expressed by

$$\left. \begin{aligned} \xi_1 &= \xi - \xi' + \eta' + \zeta', & \eta_1 &= \eta + \xi' - \eta' + \zeta', & \zeta_1 &= \zeta + \xi' + \eta' - \zeta', \\ \xi'_1 &= -\xi', & \eta'_1 &= -\eta', & \zeta'_1 &= -\zeta' \end{aligned} \right\}, \quad (\text{B})$$

which gives

$$\begin{aligned} \xi &= \xi_1 - \xi'_1 + \eta'_1 + \zeta'_1, & \eta &= \eta_1 + \xi'_1 - \eta'_1 + \zeta'_1, & \zeta &= \zeta_1 + \xi'_1 + \eta'_1 - \zeta'_1, \\ \xi' &= -\xi'_1, & \eta' &= -\eta'_1, & \zeta' &= -\zeta'_1, \end{aligned}$$

and this transformation changes the quadric (iii) into itself.

The equations (A) then transform the equations of the surfaces (i), (ii) into the forms

$$\xi'/\xi'_0 = \eta'/\eta'_0 = \zeta'/\zeta'_0$$

$$\begin{aligned} (\xi' + \eta + \zeta)/(\xi'_0 + \eta_0 + \zeta_1) &= (\xi + \eta' + \zeta)/(\xi_0 + \eta'_0 + \zeta_0) \\ &= (\xi + \eta + \zeta)/(\xi_0 + \eta_0 + \zeta_0); \end{aligned}$$

these equations can be interpreted in space of five dimensions to show that the line which they then represent passes through the point  $(\xi_0, \eta_0, \zeta_0, \xi'_0, \eta'_0, \zeta'_0)$  of the quadric (iii) and therefore only meets this quadric again in one further point; the co-ordinates of the latter are given by equations (B) above.

*It is thus shown that two of the fifteen quartic surfaces associated with two skew lines of the fundamental configuration have one point in common beside the given common point O, together with three skew lines and their common transversal, these being the lines of the original 15 not meeting the two lines with which the surfaces are associated.*

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*Atmospheric Diffusion shown on a Distance-Neighbour Graph.*

By LEWIS F. RICHARDSON.

(Communicated by Sir Gilbert Walker, F.R.S.—Received November 7, 1925.)

## § 1. THE NEED FOR A NEW METHOD.

§ 1.1. *Introduction.*

If the diffusivity  $K$  of a substance whose mass per volume of atmosphere is  $\chi$  be defined by an equation of Fick's type

$$\bar{u} \frac{\partial \chi}{\partial x} + \bar{v} \frac{\partial \chi}{\partial y} + \bar{w} \frac{\partial \chi}{\partial z} + \frac{\partial \chi}{\partial t} = \frac{\partial}{\partial x} \left( K \frac{\partial \chi}{\partial x} \right) + \frac{\partial}{\partial y} \left( K \frac{\partial \chi}{\partial y} \right) + \frac{\partial}{\partial z} \left( K \frac{\partial \chi}{\partial z} \right), \quad (1)$$

$x, y, z, t$  being Cartesian co-ordinates and time,  $\bar{u}, \bar{v}, \bar{w}$  being the components of mean velocity, then the measured values\* of  $K$  have been found to be  $0.2 \text{ cm.}^2 \text{ sec.}^{-1}$  in capillary tubes (Kaye and Laby's Tables),  $10^5 \text{ cm.}^2 \text{ sec.}^{-1}$  when gusts are smoothed out of the mean wind (Akerblom, G. I. Taylor, Hesselberg, etc.),  $10^8 \text{ cm.}^2 \text{ sec.}^{-1}$  when the means extend over a time comparable with 4 hours (L. F. Richardson and D. Proctor),  $10^{11} \text{ cm.}^2 \text{ sec.}^{-1}$  when the mean wind is taken to be the general circulation characteristic of the latitude (Defant). Thus the so-called constant  $K$  varies in a ratio of 2 to a billion. The present paper records an attempt to comprehend all this range of diffusivity in one coherent scheme.

Lest the method which I shall adopt should strike the reader as queer and roundabout, I wish to justify it by showing first why some known methods are in difficulties.

§ 1.2. *Does the Wind possess a Velocity?*

This question, at first sight foolish, improves on acquaintance. A velocity is defined, for example, in Lamb's 'Dynamics' to this effect: Let  $\Delta x$  be the distance in the  $x$  direction passed over in a time  $\Delta t$ , then the  $x$ -component of velocity is the limit of  $\Delta x/\Delta t$  as  $\Delta t \rightarrow 0$ . But for an air particle it is not obvious that  $\Delta x/\Delta t$  attains a limit as  $\Delta t \rightarrow 0$ .

We may really have to describe the position  $x$  of an air particle by something rather like Weierstrass's function, of which F. Klein gives an entertaining description ('Anwendung der Differential und Integralrechnung auf Geometrie,' Leipzig, B. G. Teubner, 1902), say,

$$x = kt + \sum_n \left(\frac{1}{5}\right)^n \cos(5^n \pi t),$$

\* For references to publications, see the table in § 5.2.



where  $k$  is independent of  $t$  and  $n$  is a positive integer. This gives a definite position  $x$  to the air particle, because the series of co-efficients  $\frac{1}{2} + \frac{1}{4} + \frac{1}{8} + \frac{1}{16} + \dots$  converges, and makes  $x$  a continuous function of  $t$ ; but it gives no limit to  $\Delta x/\Delta t$ , because, as the series proceeds, the elementary waves, while becoming shorter, become also steeper. It is not suggested that these particular periods and amplitudes, which Klein chose for illustration, have anything to do with the wind.

A general and beautiful theory of "Diffusion by Continuous Movements" has been given by G. I. Taylor.\* It is expressed in terms of velocity.

Although this theory of Taylor's is available, yet I think it will be a useful adventure to try now to make a theory of diffusion without assuming that  $\Delta x/\Delta t$  has a limit.

### § 1.3. *The Lagrangian Specification adopted. Notation for Means. Time Rate of a Mean.*

In view of the foregoing considerations, let us not think of velocity, but only of various hyphenated velocities, such as the one-minute-velocity, or the six-hours-velocity, the words attached by the hyphen indicating the value of  $\Delta t$ .

The position of a particle is, however, a continuous function of time. The Lagrangian specification of fluid motion is applicable. A particle at the point  $(a, b, c)$  at time zero, is at  $(x, y, z)$  at time  $t$ .

Following Taylor, a square bracket [ ] will be used to denote a mean value, so that  $[A]$  is the mean of any quantity  $A$ . The portion of space-time over which the mean is taken will be specified as occasion arises.

Even if  $(x - a)$  has no derivative with respect to  $t$ , yet  $[(x - a)]$  may have such a derivative. For instance, this happens with the Weierstrassian function mentioned above, if the mean is taken over a time. Let us assume that  $[(x - a)]$  has a derivative when taken over either a space or a time; for there is no evidence to the contrary.

### § 1.4. *A Search for Natural Mean Values.*

At first sight a good way of specifying diffusion would be to take the displacements  $x - a$ ,  $y - b$ ,  $z - c$  of an air particle, and to form means of their powers and products such as  $[x - a]$ ,  $[(x - a)^2]$ ,  $[(x - a)(y - b)]$ , and the like.

But observation shows that the numerical values would depend entirely upon how large a volume was included in the mean. To see this, imagine that

\* 'Proc. Lond. Math. Soc.,' Ser. 2, vol 20, Part 3 (1920).

we could introduce just two molecules of acetylene and trace their wanderings. If initially they are  $10^{-5}$  cm. apart it seems likely, judging by what is known about molecular diffusion and by what one sees of the motion of smoke, that after travelling for one second they would still be within 10 cm. of one another. If, however, the two molecules are initially  $10^{+5}$  cm. apart they may be caught in two gusts moving in rather different azimuths, so that after one second their separation may have altered by several metres.

Thus it appears that if  $y$  is a co-ordinate directed horizontally at right angles to the mean-wind so that  $[(y - b)] = 0$ , then the value obtained after a fixed time for  $[(y - b)^2]$  would increase with the range of distance normal to the wind over which the mean was taken.

Is there any type of mean that forms a natural standard? We might try—

(i) A mean over a volume so large that its exact size did not matter, a limit to  $[(y - b)^2]$  being attained. This will not do, because Defant's researches show that no limit is attained within the volume of the atmosphere.

(ii) A mean taken over a definite set of molecules. Suppose that we were to let loose a sphere 0.01 cm. in diameter of acetylene, which has much the same density as air. The sphere contains about  $10^{18}$  molecules. For the first few hundredths of a second its rate of diffusion will be the molecular one  $K = 0.2$ ; then micro-turbulence will spread it less slowly; then, after a few seconds, part may get caught in one of the gusts such as are shown by a pressure-tube anemometer, while another part may remain in a lull, so that it is torn asunder and gusts scatter it,  $K$  being  $10^4$ . Next squalls of several minutes' duration separate it more rapidly. Its rate of diffusion is now measured by  $K = 10^8$ . Then one part gets into a cyclone and another remains behind in an anti-cyclone, and its rate of diffusion is measured by Defant's value  $K = 10^{11}$ . Finally, it is fairly uniformly spread throughout the earth's atmosphere at the rate of about one molecule of acetylene for every cube of surface air 70 metres in the edge.

This diffusing dot is in a sense a natural standard. In the theory of the diffusion of heat (see, for example, E. W. Hobson, 'Encyk. Math. Wiss.', vol. 4, p. 187) something rather like this is found to be useful. A small dot of heat is imagined to spread out as time proceeds into an unbounded medium. This distribution of heat in space-time is taken as an element, like the point-charge in electrostatics, from which more complicated distributions can be built up. Can we do likewise for diffusion in the atmosphere? Imagine at an instant a gradient of concentration of acetylene in the atmosphere over an area measuring 100 km.  $\times$  100 km. Let each cube of  $10^{-2}$  cm. edge begin separately to spread

out in the manner described above, and let us superpose the separate spreadings in the hope of finding the flux of mass down the gradient of concentration. To do this we would naturally consider the change in a *short* time  $\Delta t$  of, say, 1/100 second. But in this short time each dot spreads with molecular diffusivity  $0.2 \text{ cm.}^2 \text{ sec.}^{-1}$ . So any results deduced from the superposition of the effects of the dots will correspond to molecular diffusivity and will ignore the effects of eddies. This picture is false to Nature. So we must conclude that *in the atmosphere a spreading dot will not serve as an element from which general distributions can be built up.*

§ 2. A TYPE OF MEAN WHICH AVOIDS THE FOREGOING DIFFICULTIES AND WHICH MIGHT WITH ADVANTAGE BE OBSERVED.

The fundamental idea of this paper is that the rate of diffusion increases with the distance apart. To state this carefully let us revert to the two molecules of acetylene, let loose at  $t = 0$  at the points  $(a_1, b_1, c_1)$ ,  $(a_2, b_2, c_2)$ . At time  $t$  let their positions be  $(x_1, y_1, z_1)$ ,  $(x_2, y_2, z_2)$ . The  $x$  component of their separation is initially  $a_2 - a_1$  and becomes  $x_2 - x_1$  at time  $t$ . Now let the release of a pair of particles at the same points be repeated many times in succession, and let [ ] denote a mean taken over these successive pairs. Consider the mean square of the deviation of  $(x_1 - x_2)$  from its mean at time  $t$ , that is,

$$[(x_1 - x_2) - [x_1 - x_2]]^2 = [j] \text{ say.}$$

Suppose, for example, that  $[x_1 - x_2]$  is a kilometre. Then gusts, which may be seen on a lake or on a cornfield as patches of ruffled surface a fraction of a kilometre long, would affect individual members of the pair  $x_1, x_2$  separately and so would tend to increase  $[j]$ . We should get the average effect of such gusts if we prolonged the time of averaging indefinitely. The time of averaging must not be confused with  $t$ , the time of flight. It is an advantage to have a *pair* of marked molecules. For if instead we considered molecules released one at a time, then their mean square deviation from their mean position at  $t$ , namely,  $[(x - [x])]^2$ , would depend on larger and larger eddies as the time included in the average [ ] was increased, so that no limit to the average would be attained until cyclonic changes were included. But when molecules are released in pairs this is not so. For if a cyclone passes over the district so that the wind changes its direction through one or two right angles, these changes will occur nearly simultaneously at the two stations one kilometre apart, so that they will not have much effect on individual values of  $(x_1 - x_2)$  nor on  $[j]$ . We have at last found in  $[j]$  a mean which attains a limit, as the time of averaging is prolonged

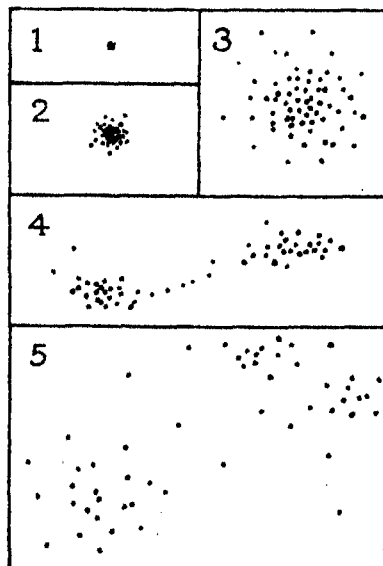
indefinitely, and yet only brings in the effects of eddies comparable in diameter with  $[x_1 - x_2]$  or less.

Direct observations of  $[j]$  have not been made so far as I know, but there is a mass of published evidence about turbulence which strongly suggests that  $[j]/t$  is independent of  $t$ , if  $t$  is neither too small nor too large, and that  $[j]/t$  increases with the distance between the starting points.

### § 3. A STATISTIC FOR CLUSTERS.

#### § 3.1. *Introduction.*

The failure of the dispersal of a point-charge to serve as a mathematical element, from which the dispersal of an extended system may be built up, appears to be intimately connected with the fact that in the atmosphere the dispersal goes on in patches. That is to say, a small dense cluster of marked molecules, represented by the dot in fig. 1 which, by molecular diffusion alone, would spread through the successive spherical clusters shown in figs. 2 and 3, actually seldom passes through the large spherical stage 3, because it is first sheared into two detached clusters as suggested in fig. 4. These are carried far from one another, and are likely to be again torn into smaller pieces as in fig. 5. Meanwhile each of the torn parts is gradually spreading by molecular diffusion. These diagrams are, of course, merely illustrative fictions.



FIGS. 1-5.

As a preliminary to describing the succession of changes, we must find out how to describe the distribution at a single instant. The problem is rather like that of finding some simple specification of the extent to which the population is divided between cities, towns, villages and isolated houses, without making a map; for in the atmosphere a map of all the eddies would be too bewilderingly complicated. We want something that gives us a general measure of the spread of the molecules, thus serving the purpose of the standard deviation of the whole aggregate of marked molecules from its mean, and yet at the same time informs us about the internal details of the cluster. Both purposes will be served, as will be shown, by the following method, which is not intended as a practical observation, but as a mathematical specification.

§ 3.2. *Definition of the Statistic Q, the Mean Number of Neighbours per Length.*

The air is supposed to contain a large number of "marked molecules." They might, for example, be acetylene. For simplicity, let us confine attention to distribution of points on a straight line. Take any marked molecule, which for reference we will call A. With A as origin, divide the line by sections at positive and negative integral multiples of a unit  $h$ , thus forming "cells" each of length  $h$ . Count the number of marked molecules in each of these cells. When a molecule is exactly on the partition between a pair of cells, half of it is attributed to each cell. Let  $h \cdot A_{n, n+1}$  denote the number in the cell between  $l = nh$  and  $l = (n+1)h$  where  $l$  is the distance from A measured in the positive sense, and  $n$  is an integer. Let there be  $N$  marked molecules altogether. A molecule might conceivably be considered to be its own neighbour at zero distance, but we do not make this convention, and therefore the sum of the numbers in the cells is  $N - 1$ . Next repeat the performance with the origin at each one of the other marked molecules B, C, D, in turn. Then form the mean

$$Q_{n, n+1} = \frac{1}{N} (A_{n, n+1} + B_{n, n+1} + C_{n, n+1} + \text{etc., to } N \text{ terms}).$$

In this way we obtain a set of quantities  $Q_{0, 1}, Q_{1, 2}, Q_{2, 3}, \dots$ , which are numbers of marked molecules per length, classified according to their distances  $l$  from other molecules; these distances lying in the ranges 0 to  $h$ ,  $h$  to  $2h$ ,  $2h$  to  $3h$ , and so on. Next, it will be well to draw a diagram in which the ordinate is  $Q_{n, n+1}$  for the range of abscissæ extending from  $l = nh$  to  $l = (n+1)h$ . We may now drop the suffixes and regard  $Q$  as a function of  $l$ . This ( $l, Q$ ) diagram has many interesting properties.

To illustrate the definition the lower part of fig. 6 was obtained by making the prescribed counts on the linear cluster of 7 molecules marked above.

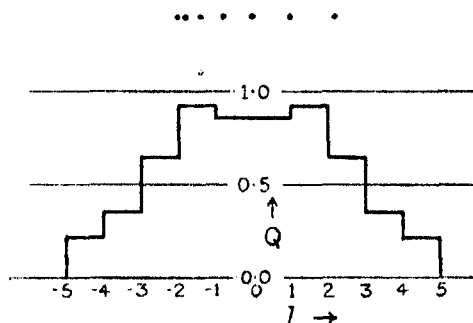


FIG. 6.

successive distances between the molecules are, in tenths, 2, 4, 6, 8, 10, 12, and  $h$  is unity.

### § 3.3. Note on the Step $h$ .

This element of length should be chosen so that in the average  $Q_{n,n+1}$  the element shall contain a considerable number, say, at least 100 marked molecules over the values of  $l$  where they are most crowded. Otherwise, random errors of sampling might become apparent. Even if this is done for most of the diagram, there may be other ranges of  $l$  where marked molecules are so scarce that sampling errors might become noticeable. On the other hand, if  $h$  were made too large the steps in the diagram might become too wide; whereas we want the stairs to look like a curve. These compromises are perfectly familiar in statistical work, and are inevitable. Although mentioned here for completeness, they are really of no importance, as we may easily have a billion molecules in the cluster. So that in future we shall replace the stairs by a curve drawn through the centre of each step. In other words, the mean number of neighbours per length, like the density, or the concentration, attains a "quasi-limit" when the element of space has a magnitude lying in a certain range.

### § 3.4. The $(l, Q)$ Diagram is Symmetrical about the $Q$ Axis.

For the distance between every pair of molecules is counted twice, as negative from one end, as positive from the other. Therefore, if  $Q$  be expanded in powers of  $l$  only even powers can occur.

§ 3.5. *As Diffusion proceeds, the Area enclosed between the  $l$  Axis and the  $(l, Q)$  Curve remains constant.*

For this area when expressed in units of  $l$  and  $Q$  is simply one less than the whole number  $N$  of marked molecules. This is easily proved from the definition of  $Q$ . And by hypothesis  $N$  remains constant.

This property of the graph suggests that  $Q$  must satisfy a differential equation of the type

$$\frac{\partial Q}{\partial t} = \frac{\partial}{\partial l} \left\{ \begin{array}{l} \text{some function of } l \text{ which attains} \\ \text{a limit as } l \rightarrow \infty \text{ equal to that} \\ \text{attained as } l \rightarrow -\infty \end{array} \right\},$$

for, if so

$$\int_{-\infty}^{\infty} \frac{\partial Q}{\partial t} dl = 0.$$

§ 3.6. *The  $(l, Q)$  Diagram exhibits the Size of a Linear Cluster.*

For if the distance between the extreme molecules at the opposite ends of the cluster be  $L$ , then  $Q$  is zero for all values of  $|l|$  greater than  $|L|$ ; and  $Q$  is finite when  $l = \pm L$ . Thus, the extreme width of the  $l, Q$  curve is twice the extreme diameter of the cluster. The relation between the standard deviations will be discussed in § 6.8.

§ 3.7. *The Changing Form of the  $(l, Q)$  Diagram as Diffusion proceeds.*

It is evident from the foregoing that if there is only one linear cluster, and it spreads along its line, the  $(l, Q)$  graph must spread along the  $l$  axis. And as the area under it must be constant, its mean height in the  $Q$ -direction must decrease.

Let us consider another very simple case (analogous to the melting of a crystal).<sup>\*</sup> Suppose that initially-marked molecules are equally spaced at intervals of one centimetre all along the line without bound in either direction. What will the  $(l, Q)$  graph look like? No molecule will have a neighbour nearer than a centimetre, so  $Q$  is zero for  $0 < l < 1$ .

At  $l = 1$  cm. neighbours are indefinitely common and  $Q$  is infinite. Again, there are no neighbours in the range  $1 < l < 2$ , and so on. The graph consists of a series of infinities of  $Q$  at  $l = \pm (1, 2, 3, 4, \dots \text{ cm.})$  with  $Q = 0$  everywhere else.

Now suppose that diffusion takes place. Can we find the changes from Fick's equation? Not from it alone, for Fick's equation is a statement about the gradients of a continuous function of position, whereas we have only particles

<sup>\*</sup> Note added December 7.

widely separated. If Fick's equation is to be applied to this special example, it would have to be by the aid of an additional hypothesis derived from the theory of probability. Instead, I get the following from memories of snow-flakes falling, of the Brownian motion under a microscope, or of foam circulating on a millpond. With these in mind, it is evident that the perfect regularity of the arrangement of marked molecules will soon be a little disturbed. Molecules will acquire neighbours a little nearer and a little farther away than the exact 1, 2, 3, 4, ... cm., and neighbours at these distances will no longer be infinitely common. That is to say, the infinities of  $Q$  will be softened down into peaks with spreading bases. In an early stage the bases will not join; there will still be no neighbours at distances, such as  $\frac{1}{2}$ ,  $1\frac{1}{2}$ ,  $2\frac{1}{2}$ , ... cms. In this stage the area enclosed between each peak and the  $l$  axis must remain constant. The form of the intermediate curve shown in fig. 7 is intended merely to suggest that flattening proceeds more rapidly as  $l$  is greater; otherwise, the curve is a guess. Later (§ 5.4, § 6.7) some other cases will be discussed quantitatively.

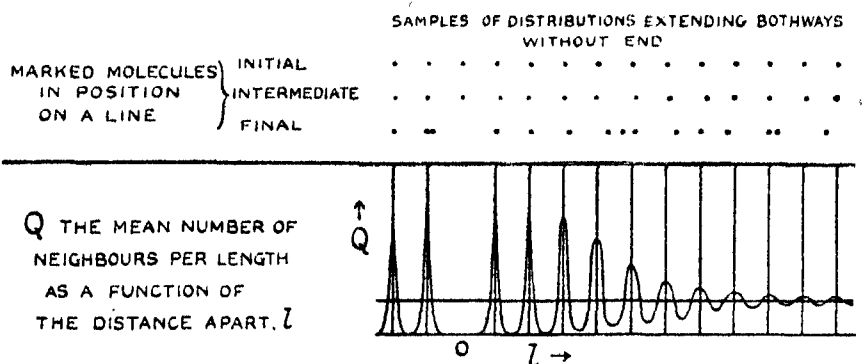


FIG. 7.

### § 3.8. *The Final State after Thorough Diffusion.*

From the foregoing we should expect the final state to be represented by a straight line parallel to the  $l$  axis. This expectation is confirmed by considerations of probability. For there seems no reason why the number  $Q$  of marked molecules per length should have any dependence upon the distance to any molecule, when the distribution is purely random.

### § 3.9. *A Failure of Concentration as a Descriptive Idea.*

In the preceding special example, if we are to speak of concentration at all, we must take a long element of length, say 1,000 cms., in order to have a good



many marked molecules in it. Then all that can be said about the concentration is that it was initially independent of position and remained so always. According to this view nothing happened. How different from the lively process shown on the  $(l, Q)$  diagram!

#### §4. FICK'S EQUATION AND THE DISTANCE-NEIGHBOUR DIAGRAM.

##### §4.1. *Introduction.*

The new theory which is intended to apply to both eddy- and molecular diffusion ought to be consistent with Fick's equation in the special case of no eddies. Let us now explore this connection.

We have seen that the idea of the "concentration" of marked molecules, given as a function of position, has in one instance signally failed to describe that which we wish to discuss. Fick's equation, being based on the idea of concentration as a function of position, has failed there also. Elsewhere we shall find both very useful.

##### §4.2. *Continuous Concentration.*

In order to bring Fick's equation into our theory we must suppose that the concentration  $v$ , defined to be the number of marked molecules per length, is a continuous function of  $x$  possessing derivatives  $\partial v/\partial x$ ,  $\partial^2 v/\partial x^2$ . This supposition is a little artificial. But it seems likely that  $\Delta v/\Delta x$  really attains with sufficient accuracy a quasi-limit when  $\Delta x$  is neither too large nor too small. Fick's equation is then

$$\frac{\partial v}{\partial t} = K \frac{\partial^2 v}{\partial x^2}.$$

Next  $Q$  must be redefined in terms of  $v$ . The definition in terms of continuous concentration can be made to agree with that in terms of particles, except as regards neighbours as close as or closer than the closest pairs of particles. As a reminder of this, often unimportant, discrepancy, the new function will be denoted by small  $q$ . For instance, if each of the particles in fig. 7 were replaced by a small dot of continuous substance, then  $q$  would have an infinity at  $l = 0$  where  $Q$  is zero.

##### §4.3. *The Definition of $q$ applicable when the Diffusing Substance is Continuous, not Molecular.*

We take any point  $x$  on the line at which the concentration is  $v$  a function of  $x$  and time only. It will sometimes be written  $v(x, t)$ . We proceed from  $x$  a further distance  $l$  to  $x + l$ . Let the concentration at  $x + l$  be  $v_1$ . Here

$v_1$ , unlike  $v$ , must be regarded as a function of three independent variables  $x$ ,  $l$  and  $t$ , and may accordingly be written  $v_1(x, l, t)$ . The analogue of  $A_{n, n+1}$  in the previous definition is here simply  $v_1$  regarded as a function of  $l$  while  $x$  is fixed. Then, because in taking the mean, each particle comes in once as origin, we must here form a weighted mean, the weight being  $v$ . We thus arrive at

$$q = \lim_{\substack{\lambda \rightarrow \infty \\ \theta \rightarrow \infty}} \frac{\int_{-\theta}^{\lambda} v(x, t) \cdot v_1(x, l, t) dx}{\int_{-\theta}^{\lambda} v(x, t) dx} \quad (1)$$

This leaves  $q$  a function of  $l$  and  $t$  only.

If there is a limit there can only be one, so that to a given function  $v(x)$  only one function  $q(l)$  as defined in this way can correspond. As we shall see later, the converse is not true.

It generally happens that the integrals in the numerator and denominator attain their limits separately, and when this occurs we can write the definition in the simpler form

$$q = \frac{1}{N} \int_{-\infty}^{+\infty} v(x, t) \cdot v_1(x, l, t) dx \quad (2)$$

where

$$N = \int_{-\infty}^{+\infty} v dx, \quad (3)$$

so that  $N$  is the whole number of marked particles as in the definition of  $Q$ .

#### §4.4. *Correspondence of Areas on the $(x, v)$ and $(l, q)$ Graphs when the Areas are Finite.*

$$\int_{-\infty}^{+\infty} q dl = \frac{1}{N} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} v(x) \cdot v_1(x, l) dx dl.$$

Since the termini are independent of one another, changing the sequence of integrations makes no difference to the result. Integrate first with respect to  $l$ . Then as the range is infinite, the inner integral transforms thus :—

$$\int_{-\infty}^{+\infty} v_1 dl = \int_{-\infty}^{+\infty} v_1 dx = \int_{-\infty}^{+\infty} v dx = N.$$

Therefore, on inserting this value of the inner integral

$$\int_{-\infty}^{+\infty} q dl = \frac{N}{N} \int_{-\infty}^{+\infty} v dx = N.$$

So

$$\int_{-\infty}^{+\infty} q dl = \int_{-\infty}^{+\infty} v dx,$$

a result which we shall often require.

§4.5. *The Differential Equation for the  $(l, q)$  Graph when the Diffusion is Fickian.*

It will now be proved that—

When there is no mean motion or eddies then  $q$ , the mean number of neighbours per length, is related to the time  $t$  and the separation  $l$  by a differential equation like Fick's, which relates the concentration  $v$  to the time  $t$  and the position  $x$ ; but for  $q$  the diffusivity is double that for  $v$ . It is assumed that  $v dv/dx$  vanishes at infinity.

If  $\Pi = vv_1$ , then because  $\partial v_1/\partial x = \partial v_1/\partial l$  and  $\partial^2 v_1/\partial x^2 = \partial^2 v_1/\partial l^2$ , it may be proved without any assumption about vanishing at infinity, or about Fick's equation, that

$$\frac{\partial^2 \Pi}{\partial x^2} - 2 \frac{\partial^2 \Pi}{\partial x \partial l} + 2 \frac{\partial^2 \Pi}{\partial l^2} = v \frac{\partial^2 v_1}{\partial x^2} + v_1 \frac{\partial^2 v}{\partial x^2}. \quad (1)$$

In view of Fick's equation, namely,

$$\frac{\partial v}{\partial t} = K \frac{\partial^2 v}{\partial x^2} \quad \text{and} \quad \frac{\partial^2 v_1}{\partial t} = K \frac{\partial^2 v_1}{\partial x^2}, \quad (2)$$

the second member of (1) transforms, into

$$\frac{1}{K} \left( v \frac{\partial v_1}{\partial t} + v_1 \frac{\partial v}{\partial t} \right) = \frac{1}{K} \frac{\partial \Pi}{\partial t}. \quad (3)$$

Thus  $v, v_1$  no longer appear separately, and their product  $\Pi$  satisfies the linear equation

$$\frac{\partial \Pi}{\partial t} = K \left\{ \frac{\partial^2 \Pi}{\partial x^2} - 2 \frac{\partial^2 \Pi}{\partial x \partial l} + 2 \frac{\partial^2 \Pi}{\partial l^2} \right\}. \quad (4)$$

Now

$$\int_{-\infty}^{\infty} \Pi \cdot dx = Nq, \quad (5)$$

and on integrating the  $\Pi$ -equation with the proviso that  $\partial \Pi/\partial x$  and  $\partial \Pi/\partial l$  both vanish as  $x \rightarrow +\infty$  and  $-\infty$  we obtain

$$\frac{\partial q}{\partial t} = 2K \frac{\partial^2 q}{\partial l^2}. \quad (6)$$

Compare this with (2) and the theorem is proved.

\* §4.6. *Theorem: The Effect of a Mean Motion independent of  $x$  disappears when the number of Neighbours per Length is related to Separation and Time.*

For, by the definition,  $q$  is independent of the choice of the origin of  $x$ , and so, if the mean velocity  $\bar{u}$  is independent of  $x$ , we can get rid of  $\bar{u}$  by giving a

\* §4.6 was added, and the corresponding alterations were made, in §5.1, §5.2, §8, on December 7.

suitable velocity to the origin of  $x$ . This can be done even if  $a$  is an arbitrary function of time.

For simplicity in § 4.5 it was assumed that there was no mean motion. Actually when  $K$  has been derived from observations of smoke or of balloons, the mean velocity has customarily been taken into account by using as the definition of  $K$  some equation more or less equivalent to §1.1 (1), in which  $\bar{u}$ ,  $\bar{v}$ ,  $\bar{w}$  appear.

We see now that

$$\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} = K \frac{\partial^2 v}{\partial x^2} \quad (1)$$

leads to

$$\frac{\partial q}{\partial t} = 2K \frac{\partial^2 q}{\partial l^2}, \quad (2)$$

in which  $\bar{u}$  does not appear.

Incidentally it is of interest to take the form (1) in place of § 4.5 (2) in forming the  $\Pi$ -equation. We thus obtain

$$\frac{\partial \Pi}{\partial t} + u \frac{\partial \Pi}{\partial x} = K \left\{ \frac{\partial^2 \Pi}{\partial x^2} - 2 \frac{\partial^2 \Pi}{\partial x \partial t} + 2 \frac{\partial^2 \Pi}{\partial t^2} \right\}, \quad (3)$$

and, on integration with respect to  $x$ , the term in  $\bar{u}$  vanishes if  $\Pi$  has the same value for all indefinitely great values of  $|x|$ . Thus we arrive again at equation (2) of the present section.

§ 4.7. \* *The Present Theory, written for Diffusion on a Straight Line, is applicable also to the Projection of Three-dimensional Diffusion on to this Straight Line.*

For let  $\rho$  be the number of marked molecules per volume, and let them be diffusing according to

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial x} \left( K \frac{\partial \rho}{\partial x} \right) + \frac{\partial}{\partial y} \left( K \frac{\partial \rho}{\partial y} \right) + \frac{\partial}{\partial z} \left( K \frac{\partial \rho}{\partial z} \right). \quad (1)$$

Now project each molecule normally on to the  $x$ -axis, and let  $v'$  be the number of projections per length. Then

$$v' = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \rho \, dy \, dz. \quad (2)$$

Let us assume that  $\rho$  vanishes at infinity in such a way as to make  $v'$  finite. On integrating (1) with respect to  $y$  and  $z$  so as to produce an equation in  $v'$ , the term  $\frac{\partial}{\partial y} \left( K \frac{\partial \rho}{\partial y} \right)$  yields

$$\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \left[ K \frac{\partial \rho}{\partial y} \right] dy \, dz,$$

\* § 4.7 and consequent explanations elsewhere were added on December 7.

and we may usually safely assume that the integrand vanishes. The term

$\frac{\partial}{\partial z} \left( K \frac{\partial \rho}{\partial z} \right)$  behaves similarly. Thus there results

$$\frac{\partial v}{\partial z} = K \frac{\partial^2 v}{\partial x^2}. \quad (3)$$

This is the interpretation that must always be given to the present theory before it can be applied to observations.

## § 5. NON-FICKIAN DIFFUSION.

### § 5.1. *Generalisation for Atmospheric Eddies.*

When the diffusion is molecular both equations § 4.6 (1) and § 4.6 (2) correctly describe it. When the eddies of the free atmosphere come into action neither of these two equations describe the phenomena correctly; but whereas in Fick's equation the defect appears to be incurable, it is very easily remedied in the new equation now presented. That is to say, the chief advantage of the variables  $l$  and  $q$ , to which all the foregoing is merely preparatory, appears when we consider the effects of eddies. For, as already stated, observation shows that the rate of diffusion increases with the separation  $l$  of neighbours. We can represent this by writing

$$\frac{\partial q}{\partial t} = \frac{\partial}{\partial l} \left( F(l) \cdot \frac{\partial q}{\partial l} \right), \quad (1)$$

where  $F(l)$  is an increasing function of  $l$ . In passing it should be noted that it would not do to write the second member  $F(l) \cdot \partial^2 q / \partial l^2$ , for then  $\int_{-\infty}^{+\infty} \frac{\partial q}{\partial t} dl$  would not necessarily vanish and the total number of particles would not be fixed.

If we were to modify Fick's equation by writing

$$\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} = \frac{\partial}{\partial x} \left( f(x) \cdot \frac{\partial v}{\partial x} \right)$$

that would mean that the diffusivity depended on position, an effect altogether different from the one represented by  $F(l)$ , and one which will not be studied in this paper. Instead, the paper discusses an atmosphere in which the diffusivity is independent of position, but depends on separation.

### § 5.2. *Reduction of Existing Observations.*

Let us next consider some observations which show how  $F(l)$  depends on  $l$ . The observations have been made for other purposes, and are not quite what

is desirable here. The quantity usually measured has been  $K$  in the equation § 1.1 (1) or something equivalent.

In accordance with § 4.5 (6),  $F(l)$ , if it were merely a constant, would be equal to  $2K$ . Actually, many values of  $l$  co-operate in the diffusion, but those which are largest not only produce most diffusion, but also have most weight in determining  $K$ , when  $K$  is calculated from the mean *squared* deviation from the mean. Thus, it seems likely that we shall get the right order of magnitude both for  $F(l)$  and  $l$ , if we put  $F(l)$  equal to  $2K$  and  $l$  equal to the standard deviation of the particles from their mean. As  $l$  varies in the ratio  $1 : 10^9$ , even very crude estimates of  $F(l)$  show its relation to  $l$  quite clearly.

When  $K$  has been obtained from the variation of wind with height,  $2K$  is still assumed to be roughly equal to  $F(l)$  and the corresponding  $l$  is taken to be the mean vertical separation of the anemometers that were used in finding the second derivatives of the wind-components with respect to height. When the observations were obtained from pilot balloons, we know that  $l$  cannot be less than the vertical displacement of a balloon between two sightings, so that  $l$  will probably not be less than 100 metres. On the other side  $l$  cannot be greater than the height of the observation above the ground. The mean of these two distances has been taken to be  $l$ .

The distance at which molecular motion is the chief cause of diffusion in free air may be roughly estimated in the following way:—Suppose that a very thin lamina of marked molecules could be produced in still air. The concentration should be arranged to be greatest in the central sheet and to diminish towards the outer sheets according to the law of error. The thickness of the lamina, as measured by a standard deviation from the mean, would then increase so that\*

(standard deviation) =  $\sqrt{(2Kt)}$  where  $t$  is the time from indefinite thinness.

Now, the value of  $K$  due to molecular diffusion is about  $0.17 \text{ cm.}^2 \text{ sec.}^{-1}$ . Hence, we have the following:—

time in seconds	..	..	..	..	..	0	0.001	0.01	0.1	1
thickness as measured by standard deviation, cms.						0	0.018	0.058	0.18	0.58

These numbers show clearly that molecular diffusion is very effective when the lamina is 0.01 cm. thick and much less so when it is 0.1 cm. thick. Now, if we look at cigarette smoke in the open air and ask ourselves at what separation molecular motion will produce rather more effect than the eddies, it is not difficult to make a guess. I put it at  $l = 5 \times 10^{-2} \text{ cm.}$  The integral power of ten is really all that matters.

\* 'Phil. Trans.,' A, vol. 221, p. 6 (1920).

The data are summarised in the following table :—

Reference.	$K$ cm. <sup>3</sup> sec <sup>-1</sup>	$l$ cm.
K from molecular diffusion of oxygen into nitrogen (Kaye and Laby's 'Physical and Chemical Constants'). For $l$ see preceding discussion.	$1.7 \times 10^{-1}$	$5 \times 10^{-2}$
K at 9 metres above ground from anemometers at heights of 2, 16 and 32 metres (W. Schmidt, 'Wien. Akad. Sitzb.', IIa, vol. 126, p. 773 (1917)).	$3.2 \times 10^3$	$1.5 \times 10^3$
K from anemometers at heights of 21 to 305 metres (Åkerblom, F., 'Nova Acta Reg. Soc. Upsaliensis' (1908)).	$1.2 \times 10^5$	$1.4 \times 10^4$
K from pilot balloons at heights between 100 and 800 metres (Taylor, 'Phil. Trans.', A, vol. 215, p. 27 (1914), also Hesselberg and Sverdrup, 'Leipzig Geophys. Inst.', Ser. 2, Heft 10 (1915)).	$6 \times 10^4$	$5 \times 10^4$
K from tracks of balloons either manned (L. F. Richardson, 'Weather Prediction by Numerical Process,' p. 221) or not manned (Richardson & Proctor, 'Royal Meteorological Society Memoirs,' No. 1).	$10^8$	$2 \times 10^4$
Volcano ash, same reference as last .....	$5 \times 10^8$	$5 \times 10^4$
Diffusion due to cyclones regarded as deviations from the mean circulation of the latitude (Defant, 'Geog. Ann.', H. 3, also (1921), 'Wien. Akad. Wiss. Sitzb.', IIa, vol. 130, p. 401 (1921)).	$10^{11}$	$10^8$

Since, when not obstructed by the ground, smoke spreads about as much horizontally as it does vertically,\* the observations at the smaller values of  $l$ , though made in the vertical, can be treated as applicable to the horizontal. Thus the whole collection is coherent.

The logarithms of  $K$  and  $l$  when plotted on a graph (fig. 8) are seen to lie close to a line of slight curvature. It is hardly worth while to discuss details until observations have been made in a manner appropriate for the determination of  $F(l)$  rather than of  $K$ . How such observations could be obtained will be discussed in § 7.

The straight line on the logarithmic diagram which corresponds to  $K = 0.2 l^{4/3}$  also fits the observations almost as well as the curve in the limited range between  $l =$  a metre and  $l =$  10 kilometres. For mathematical simplicity this formula will be used in the illustrations which follow.

Thus in this range  $F(l) = 0.4 l^{4/3}$  approximately, when the units are centimetres and seconds.

\* G. I. Taylor.

The equation for the changes in the  $(l, q)$  graph is then

$$\frac{\partial q}{\partial t} = \varepsilon \frac{\partial}{\partial l} \left( l^{1/3} \frac{\partial q}{\partial l} \right), \quad (1)$$

where the constant  $\varepsilon$  is of the order of  $0.4 \text{ cm.}^{2/3} \text{ sec}^{-1}$ . This equation summarises the subject.

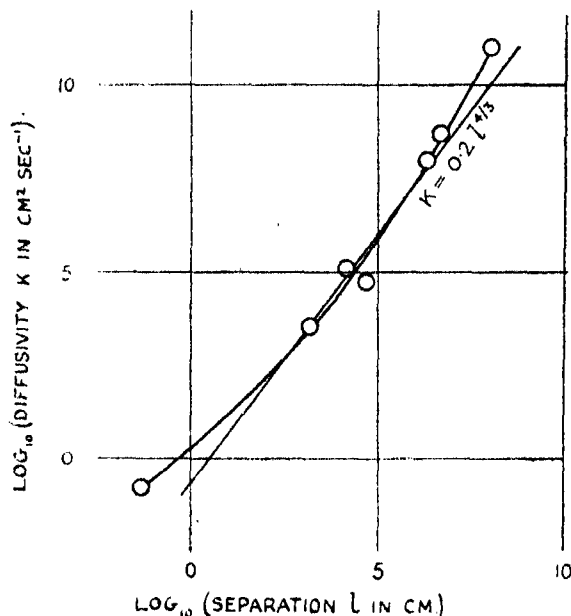


FIG. 8.

### § 5.3. *Analogy with the Diffusion of Heat.*

The fundamental equation § 5.2(1) can be brought into touch with some standard mathematical forms by changing the variable  $l$  to  $l^{1/3} = \alpha$  say. For this transforms the equation into

$$\frac{\partial q}{\partial t} = \frac{\varepsilon}{9} \left\{ 2 \frac{\partial q}{\partial \alpha} + \frac{\partial^2 q}{\partial \alpha^2} \right\}, \quad (1)$$

which is Fourier's equation for the diffusion of heat in a homogeneous solid, where the isothermal surfaces are concentric spheres of radius  $\alpha$ , and the diffusivity is  $\varepsilon/9$ . The equivalence of the equations in  $\alpha$  and  $l$  is complete, except at  $l = 0$ , where a source of sink might occur. In choosing a solution we must be sure whether it makes the whole number of marked molecules independent of time.



### § 5.4. *Non-Fickian Diffusion of an Initial Point-Cluster on a Line.*

A solution due to Fourier,\*

$$q = A (4t\epsilon/9)^{-3/2} \cdot e^{-\frac{\alpha^2}{4t\epsilon/9}}, \quad (1)$$

in which  $A$  is independent of  $t$  and  $\alpha$ , represents a process in which at  $t = 0$  all neighbours are indefinitely close, and as time proceeds they spread out continually. The corresponding value of  $N$  is

$$N = \int_{-\infty}^{+\infty} q \, dl = A (4t\epsilon/9)^{-3/2} \int_{\alpha^2 \rightarrow -\infty}^{\alpha^2 \rightarrow \infty} e^{-\frac{\alpha^2}{4t\epsilon/9}} \cdot 3\alpha^2 \cdot d\alpha.$$

Putting

$$\beta^2 = \frac{\alpha^2}{4t\epsilon/9}$$

it is found that

$$N = 3A \int_{-\infty}^{+\infty} e^{-\beta^2} \beta^2 \, d\beta. \quad (2)$$

Thus  $N$  is independent of time, as required, and there is no source at  $l = 0$ , except at  $t = 0$ .

Fig. 9 exhibits this function in the special form

$$q = 10^5 \cdot t^{-3/2} \cdot e^{-\frac{l^2\pi}{4t\epsilon/9}} \quad (3)$$

when  $\epsilon$  is given its observed value of 0.4 C.G.S. units.

At  $t = 0$  the graph would consist of an infinity of  $q$  at  $l = 0$ , and  $q = 0$  elsewhere. One graph shows the distribution at  $t = 100$  seconds. Neighbours as distant as 4 metres are now not scarce. Five minutes later, at  $t = 400$  seconds, neighbours at 40 metres are noticeable. In the corresponding distribution in space the isopleths of concentration are parallel planes. The standard deviation of the marked molecules from their mean position will be investigated in § 7.1.

## § 6. RETURNING FROM NUMBER OF NEIGHBOURS AS A FUNCTION OF SEPARATION TOWARDS CONCENTRATION AS A FUNCTION OF POSITION.

### § 6.1. *Introduction.*

In the course of the theory we began with concentration  $v$  given as a function of position  $x$ . We wished to know what became of the distribution when

\* See E. W. Hobson, 'Wärmeleitung, Encyk. Math. Wiss.,' vol. 4, p. 195.

diffusion occurred. Fick's equation being contrary to the facts, and no suitable adjustment of it being in sight, we had to change the variables from  $(x, v)$  to separation  $l$ , and mean number of neighbours per length  $q$ . This was easily done. Then the equation  $\frac{\partial q}{\partial t} = \epsilon \frac{\partial}{\partial l} \left( l^{1/2} \frac{\partial q}{\partial l} \right)$  gave the changes in the  $(l, q)$  graph. But, after all, it is  $v$  as a function of  $x$  that we should like to know; so that, after the diffusion has occurred, we wish, if possible, to change the variables  $(l, q)$  back again to  $(x, v)$ . This is not so easy, and can only be done in part.

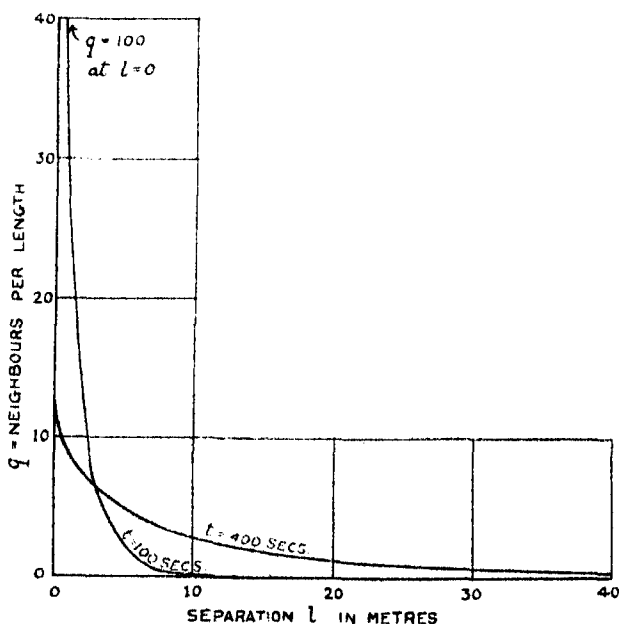


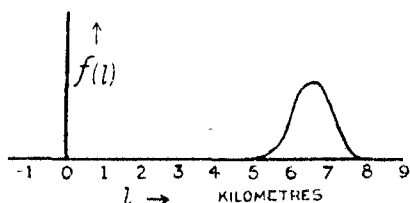
FIG. 9.

As with the problem of integration, a general method is lacking, and so it seems desirable to give typical examples and a variety of processes suited to different circumstances.

It would be too much to expect that the  $(l, q)$  graph should give us enough information to allow the distribution of particles in space to be reconstructed in all its details. For the process of taking a mean has been used in forming  $q$  to get rid of a superabundance of detail. The process is irreversible. We cannot evolve the detail again from the mean.

The origin of  $x$  is not represented by anything in the  $(l, q)$  graph.

§ 6.2. *Not every Even Function  $f(l)$  which is Positive for all Values of  $l$  can serve for the Number of Neighbours per Length.*



Try, for instance, to imagine how the population could be distributed on a line so as to produce a  $(l, Q)$  diagram like fig. 10. If you have neighbours at many distances lying between 5 and 8 km., some of them must have neighbours at distances less than 3 km., so the diagram would have to have a central hump. As drawn it cannot be an  $(l, Q)$  diagram.

However, when, as usual,  $q_B$  has been produced by diffusion from  $q_A$ , and  $q_A$  corresponded to  $v_A$ , then if the mathematics fits the physics, as it appears to do, there must exist a  $v_B$  corresponding to  $q_B$ .

### § 6.3. *The Central Value of $q$ .*

This is evidently  $q(0) = \frac{1}{N} \int_{-\infty}^{+\infty} v^2 dx$  when  $v$  vanishes at infinity.

### § 6.4. *Uniformity.*

Given that  $v = b$  a quantity independent of  $x$ .

Therefore  $v_1(x, l) = b$  also.

And by the definition of § 4.3

$$q = \text{Limit}_{\substack{\theta \rightarrow \infty \\ \lambda \rightarrow \infty}} \frac{b^2 \int_{-\theta}^{\theta} dx}{b \int_{-\theta}^{\theta} dx} = b.$$

So  $q$  is independent of  $l$ .

As to the converse, see under Fourier series.

### § 6.5. *A Single Linear "Town."*

Given that

$$v = \frac{1}{\sqrt{(2\pi)}} e^{-\frac{1}{2}x^2}.$$

Then

$$N = \int_{-\infty}^{\infty} v dx = 1.$$

Also

$$vv_1 = \frac{1}{2\pi} e^{-\frac{1}{2}\{(x+l)^2 + x^2\}} = \frac{1}{2\pi} e^{-\frac{1}{2}(\sqrt{2}x + (l/\sqrt{2}))^2} \cdot e^{-\frac{1}{2}(l^2/2)}.$$

Therefore

$$\begin{aligned}\int_{-\infty}^{\infty} v v_1 dx &= \frac{1}{\sqrt{(2\pi)}} e^{-(l^2/4)} \frac{1}{\sqrt{2} \cdot \sqrt{(2\pi)}} \int_{-\infty}^{+\infty} e^{-\frac{1}{2}(\sqrt{2}x + l/\sqrt{2})^2} d\left(\sqrt{2}x + \frac{l}{\sqrt{2}}\right) \\ &= \frac{1}{2\sqrt{\pi}} e^{-(l^2/4)} = q.\end{aligned}$$

See also a note at the end of § 6.7.

### § 6.6. Expansion in a Fourier Series.

There may be distributions of concentration, extending indefinitely in both directions, for treating which Fourier series will be suitable.

Let

$$v(x) = \frac{1}{2}A_0 + \sum_{n=1}^{n \rightarrow \infty} \{A_n \cos nx + B_n \sin nx\}, \quad (1)$$

$n$  being a positive integer and the constant  $A_0$  being so chosen as to make  $v$  everywhere positive. Then it may be shown that

$$\begin{aligned}q &= \text{Limit}_{\substack{\lambda \rightarrow \infty \\ \theta \rightarrow \infty}} \frac{\frac{1}{2}(\theta + \lambda) \left\{ \frac{A_0^2}{2} + \sum (A_n^2 + B_n^2) \cdot \cos n\lambda \right\} + \text{finite terms}}{\frac{1}{2}A_0(\theta + \lambda) + \text{finite terms}} \\ &= \frac{1}{2}A_0 + \frac{1}{A_0} \sum_{n=1}^{n \rightarrow \infty} (A_n^2 + B_n^2) \cos n\lambda.\end{aligned} \quad (3)$$

The fundamental wave-length in  $q$  and  $v$  has been taken as  $2\pi$ . Any other value could be introduced by changing the units of  $x$  and  $l$  in the same ratio, and the relations between  $A_n$ ,  $B_n$  and  $C_n$  would remain as stated.

In particular if  $q = \frac{1}{2}C_0$  simply, then  $v = q$  is a solution, and on account of the generality of the Fourier series it appears to be the only possible one.

### § 6.7. The Correspondence of Diffusion from Points on the $x$ and $l$ Axes.

Time is not involved in the connection between the position-concentration graph and the distance-neighbour graph; but we can bring in time as an aid to finding the connection. Suppose, for example, that the diffusing substance is initially concentrated in five masses each consisting of  $n$  particles near five equidistant points on the  $x$ -line at intervals  $b$  of  $x$ . Then there are neighbours near  $l = 0, \pm b, \pm 2b, \pm 3b, \pm 4b$ , but for no other values of  $l$ . The relative numbers of neighbours in these five classes are easily counted.

Next, suppose that Fickian diffusion occurs. Both graphs change, but at

the same instant they must always correspond to one another. Fig. 11 shows the two graphs at one instant.

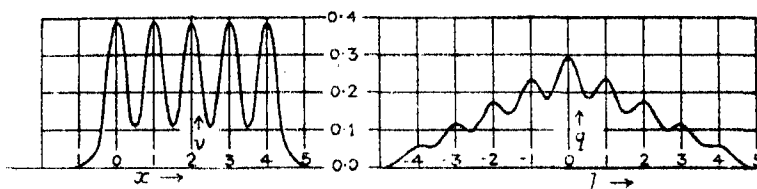


FIG. 11.

Now, a given distribution of  $v$  in  $x$  may be seen from the definition of  $q$  to lead to a unique function  $q$  of  $l$ . Thus,  $q(l)$  does not depend on how  $v(x)$  came to be, but only on what  $v(x)$  is. We have arrived at the correspondence in this example by Fickian diffusion. But if the same  $v(x)$  had been produced by non-Fickian diffusion, or in any other way, it would correspond to the same  $q(l)$ .

The simpler problem of § 6.5 may also be solved in this way.

#### § 6.8 Moments. Standard Deviation.

Formulae are usually fitted to frequency curves by way of moments (*vide* Karl Pearson, 'Biometrika,' vol. I, p. 263). Consider, therefore,

$$\frac{1}{N} \int_{-\infty}^{+\infty} l^n \cdot q \, dl = \mu_n, \text{ say,} \quad (1)$$

which is the " $n$ th moment-coefficient" of the  $q(l)$  distribution about its mean  $l = 0$ .

We shall treat only the case in which  $N$  and all the moment-integrals are finite, as occurs when  $q$  and  $v$  vanish entirely in the outer regions.

Therefore, in accordance with the definition of  $q$  in § 4.3,

$$\mu_n = \frac{1}{N^2} \int_{l=-\infty}^{l=+\infty} l^n \int_{x=-\infty}^{x=+\infty} v(x) \cdot v_1(x, l) \, dx \, dl. \quad (2)$$

Now, the limits of integration are independent of one another, so that we may change the sequence of integrations without changing anything else. Let us integrate first with respect to  $l$ , remembering that  $\rho(x)$  is independent of  $l$ . Therefore

$$\mu_n = \frac{1}{N} \int_{x=-\infty}^{x=+\infty} v(x) \left\{ \int_{l=-\infty}^{l=+\infty} \frac{1}{N} v_1(x, l) \cdot l^n \, dl \right\} dx. \quad (3)$$

Since  $v_1$  is the concentration at the point  $(x + l)$ , the inner integral is the  $n$ th moment-coefficient of the distribution of concentration taken about the point  $x$ . On comparing equations (1) and (3) it is seen that:—

*the  $n$ th moment-coefficient of the distribution  $q(l)$  of neighbours, about its centre  $l = 0$ , is the mean of the  $n$ th moment-coefficients of the distribution of marked molecules taken about every marked molecule in turn.* (4)

Since  $q(l)$  is an even function of  $l$  its moments of odd order about  $l = 0$  all vanish. That is,

$$0 = \mu_1 = \mu_3 = \mu_5 = \mu_7, \text{ etc.} \quad (5)$$

For the even moments the expression can be simplified. The most interesting case is  $n = 2$ . Let  $x_m$ , the centre of the distribution  $v(x)$ , be defined as usual by the equation

$$\int_{-\infty}^{+\infty} v(x) \cdot (x - x_m) dx = 0. \quad (6)$$

There is a familiar theorem in mechanics concerning radii of gyration round parallel axes. In like manner it can be proved that if  $\sigma_m^2$  be the second moment-coefficient of  $v(x)$  about the centre  $x_m$  and  $\sigma_x^2$  be that about any other point  $x$ , then

$$\sigma_x^2 = \sigma_m^2 + (x - x_m)^2. \quad (7)$$

From (7) and (4) it follows that

$$\begin{aligned} \mu_2 &= \frac{1}{N} \int_{-\infty}^{+\infty} v(x) \cdot \{\sigma_m^2 + (x - x_m)^2\} dx \\ &= 2\sigma_m^2. \end{aligned} \quad (8)$$

Now the standard deviations of  $q(l)$  and  $v(x)$  are respectively  $\sqrt{\mu_2}$  and  $\sigma_m$ . Hence, we have proved that: *the standard deviation of the  $q(l)$  area from its centre  $l = 0$  is  $\sqrt{2}$  times the standard deviation of the marked molecules from their centre  $x_m$ .* A glance at the distance-neighbour graph thus gives us a good impression of the size of the cluster on the line.

The skewness of the  $v(x)$  distribution is not given us by the  $(l, q)$  graph, because skewness depends upon a moment of odd order. But the higher even moments could be found. For the fourth moment-coefficient I find

$$\frac{1}{N} \int_{-\infty}^{+\infty} v(x) \cdot (x - x_m)^4 dx = \frac{1}{2} \mu_4 = \frac{3}{2} \mu_2^2. \quad (9)$$

The proof of this is omitted for brevity.

### § 7. THE DETERMINATION OF THE DIFFUSIVITY BY OBSERVATION.

§ 7.1. *The Standard Deviation of a Linear Cluster formed by Diffusion on a Straight Line from a Point, the Diffusivity for Neighbours being  $F(l) = \epsilon l^{4/3}$ , where  $\epsilon$  is independent of  $l$ . The Determination of  $\epsilon$  from Observations.*

It has already been proved in § 5.3 and § 5.4 that under these circumstances we have  $q$  given by § 5.4 (1).

To find the second moment  $\mu_2$  which is defined in § 6.8 (1), put, as before,

$$\frac{\alpha^2}{4t\epsilon/9} = \beta^2. \quad (1)$$

Then it may be shown that

$$\mu_2 = 3A (4t\epsilon/9)^3 \int_{-\infty}^{\infty} e^{-\beta^2} \beta^2 d\beta. \quad (2)$$

Now if we denote

$$\int_{-\infty}^{\infty} e^{-\beta^2} \beta^n d\beta \text{ by } S_n \quad (3)$$

it may be proved by integration by parts that

$$S_n = \frac{2}{n+1} S_{n+2}. \quad (4)$$

Also it is well known that  $S_0 = \sqrt{\pi}$ . And so

$$S_8 = \frac{7 \times 5 \times 3 \times 1}{2 \times 2 \times 2 \times 2} \sqrt{\pi} = \frac{105}{16} \sqrt{\pi} = 11.63. \quad (5)$$

Also for finishing the calculation of  $N$  which was begun in § 5.4 we shall need

$$S_2 = \frac{1}{2} \sqrt{\pi} = 0.886. \quad (6)$$

With these substitutions it follows that

$$\mu_2 = \frac{3A (4t\epsilon/9)^3 \frac{105}{16} \sqrt{\pi}}{3A \frac{1}{2} \sqrt{\pi}} = (4t\epsilon/9)^3 \frac{105}{16}. \quad (7)$$

But by the theorem (§ 6.8 (8)) of the previous section  $\sigma_m$ , the standard deviation of the marked molecules from their mean position on the line is  $\sqrt{(\frac{1}{2}\mu_2)}$ .

So

$$\sigma_m = \sqrt{\left\{ (4t\epsilon/9)^3 \frac{105}{32} \right\}} = \left( \frac{70}{243} \right)^{1/2} (\epsilon t)^{3/2}. \quad (8)$$

Or solving for  $\epsilon$

$$\epsilon = \left( \frac{243}{70} \right)^{2/3} \frac{\sigma_m^2}{t} = 1.51 \frac{\sigma_m^2}{t}. \quad (9)$$

This formula enables the coefficient  $\epsilon$  in the diffusivity for neighbours  $\epsilon l^{4/3}$  to

be determined from the scatter of particles on a straight line. The particles will really move in three dimensions, but the formula can be applied to their projections on the line, as was shown in § 4.7.

Suppose now that the formulæ we have thus deduced from the non-Fickian diffusion of neighbours with diffusivity  $\epsilon l^{4/3}$  represents the true sequence of events, but that the observations have been reduced instead by the formula\* which is a necessary consequence of the Fickian diffusion of concentration with constant diffusivity  $K$ , namely,

$$K = \frac{\sigma_m^2}{2t}, \quad (10)$$

what values will be obtained for  $K$ ?

Eliminating  $t$  between equations (9) and (10) it is found that

$$K = \frac{1}{2} \left( \frac{70}{243} \right)^{1/3} \cdot \epsilon \cdot \sigma_m^{4/3} = 0.330 \epsilon \sigma_m^{4/3}. \quad (11)$$

This shows that  $K$ , obtained in this way, will increase as the  $4/3$  power of the size  $\sigma_m$  of the scatter, as, in fact,  $K$  does (see fig. 8).

If we regard  $F(l)$  as what we wish to find from published values of  $K$ , then we must put

$$F(\sigma_m) = \epsilon \sigma_m^{4/3} = \frac{K}{0.330} 3.03 K. \quad (12)$$

As a necessary preliminary to finding out that  $F(l)$  was nearly of the form  $\epsilon l^{4/3}$  I made, in § 5.2, the guess that we should obtain the right order of magnitude for  $F(l)$  and  $l$  by putting  $F(l) = 2K$  and  $l = \sigma_m$ . These imply that  $F(\sigma_m) = 2K$ . It is seen that the guess is amply justified.

But we may now revise the value of  $\epsilon$  from  $0.4$  to  $0.4 \times 3/2 = 0.6 \text{ cm.}^2/\text{sec.}^{-1}$ . This is only a mean value roughly applicable under average circumstance in the range one metre  $< l < 10$  kilometres. A more detailed study will reveal variations of 10 times or more in  $\epsilon$  according to the up-gradients of temperature and mean-wind and other circumstances. Even so,  $\epsilon$  will be remarkably more constant than the diffusivity  $K$  for concentration, which, as we have seen, varies with  $l$  about a billion times.

\* This formula was deduced by Einstein in connection with the Brownian motion ('Ann. der Phys.,' vol. 17 (1905)). Something like it was employed by G. I. Taylor for reducing the Scotia kite ascents ('Phil. Trans.,' A, vol. 215, p. 10). The formula was given explicitly and much used by the present writer in "Some Measurements of Atmospheric Turbulence" ('Phil. Trans.,' A, vol. 221). In the latter paper there are two independent proofs of the formula, one of which in Section IV is a correct deduction from Fick's equation, the other in Section V is quite spoilt, alas, by a wrong sign in equation 3, p. 9, and a risky assumption about correlations. This error affects equation (32) on pp. 15 and 27 of the aforesaid paper, but the rest of the paper holds good independently.



Various observers (Dobson, Richardson, Roberts) have separately noted the fact that the width of an individual trail of smoke from a point source, when measured by its standard deviation  $\sigma_m$  from its mean line, is such that  $\sigma_m$  is roughly proportional to  $l^{1/2}$ . This implies that the diffusion is Fickian in certain short ranges of  $l$ , the diffusivity for neighbours  $F(l)$  being there independent of  $l$ . When an enormously wider range of  $l$  is considered we have seen that  $F(l)$  is proportional to  $l^{4/3}$  roughly.

[*Note added December 7, 1925.*—The observations collected by Richardson and Proctor in the range  $\sigma_m = 3$  km. to 86 km. fit well with the slope of the smooth curve in fig. 8.

These apparently contradictory facts may perhaps be reconciled if we regard variations in  $K$ , defined by §1.1 (1), as being due to variations in the type of mean chosen in forming  $\bar{u}$ ,  $\bar{v}$ ,  $\bar{w}$  in the same equation. As long as the mean is always taken over the same length and time,  $K$  may well be more or less constant.]

§7.2. *Theory of a Second Method by which the Diffusivity  $F(l)$  might be observed.*

It has just been shown that the value of  $\epsilon$  in  $\epsilon l^{4/3} = F(l)$  can be extracted from observations made with a wide range of  $l$  all in operation together. While this is possible mathematically, it seems, from the standpoint of practical physics, to mix too many phenomena and unnecessarily to assume that  $\epsilon$  is independent of  $l$ . It would be better to observe separately at or near each selected  $l_0$ . This can be done by a process which will be derived from the non-Fickian equation

$$\frac{\partial q}{\partial t} = \frac{\partial}{\partial l} \left\{ F(l) \frac{\partial q}{\partial l} \right\}.$$

Suppose that the "marked molecules" are initially concentrated in two plane parallel laminae, distant  $l_0$  from one another and similar to one another. The neighbour-distance diagram then consists of three sharp peaks, as suggested qualitatively in fig. 12. The central peak shows the very close neighbours

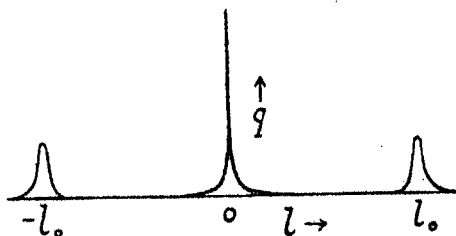


FIG. 12.

which each marked molecule has in its own lamina. The lateral peaks show the neighbours in the other lamina. The spreading of the central peak will go on very much as if there were only a single lamina (§5.4, §7.1), and does not concern us now. If the laminae are observed during a time such that they spread through only a small fraction of  $l_0$ , then we may regard  $F(l)$  as a constant and equal to  $F(l_0)$  in this short range of  $l$ , and may write accordingly

$$\frac{\partial q}{\partial t} = F(l_0) \cdot \frac{\partial^2 q}{\partial l^2}.$$

An appropriate solution of this equation is

$$q = At^{-\frac{1}{2}} e^{-\frac{(l-l_0)^2}{4tF(l_0)}},$$

which implies that the peak on the  $(l, q)$  diagram has the form of the normal curve of error,  $q$  playing the part of the "frequency." The standard deviation of the curve from its mean  $l_0$  is  $\{2tF(l_0)\}^{1/2}$ .

In determining the standard deviation from the observations it is, of course, essential that the individual values of  $(l - l_0)^2$  should be weighted in the proper way. On referring back to the definition of  $Q$  in §3.2 it is seen that we must form every possible pair of marked molecules, one from each lamina, so obtaining a set of distances  $l$ . Let  $[ ]_Q$  denote the mean for all members of the set. Then in ordinary circumstances  $[l]_Q = l_0$ . We next form the mean squared deviation from the mean and thus find

$$F([l]_Q) = \frac{[(l - [l]_Q)^2]}{2t}. \quad (1)$$

In practice the "marked molecules" could be replaced by balloons, for those values of  $l_0$  which are many times the diameter of a balloon. This is so because  $F(l)$  increases notably with  $l$ . C. H. Ley\* has invented a valve which allows a balloon to rise to a pre-arranged height and then lets out some gas so that the balloon ceases to move through the air. That is the type of apparatus required.

When there are only one or two observers, they could not manipulate many balloons at once, but they might observe pairs of balloons on successive days. Let us try to adapt the observation to this situation. Imagine first, for the sake of the argument, that the observation with many balloons arranged initially in two parallel laminae  $l_0$  apart, is made, and let us denote  $(l - l_0)^2$  by  $p$

\* 'Quart. Journ. Roy. Meteor. Soc.,' p. 247 (1911).

for short. Thus many values of  $p$  are obtained on one occasion. Next imagine that this observation were repeated once a day for a year, the time  $t$  being in all cases the same; and not too small nor too large. In this way a double set of values of  $p$  is obtained, thus:—

Days.	Pairs on one day $\longrightarrow$				
$\downarrow$	$p_{11}$	$p_{12}$	$p_{13}$	$p_{14}$	...
	$p_{21}$	$p_{22}$	$p_{23}$	...	
	$p_{31}$	$\vdots$	$\vdots$		
	$\vdots$				

The mean value of  $F(l_0)$  for all these observations is  $F(l_0) = [p]_{QS}$  the double suffix denoting the double mean, Q for rows, S for columns. We cannot proceed further without making the assumption that we obtain the general mean of  $p$  if we select at random one value of  $p$  from each row of the double set and take the mean of them. This looks passable.

If so

$$F(l_0) = \frac{[p]_S}{2t},$$

which can be determined by flying a pair of balloons on each of the many days.

This measure of atmospheric diffusion is in agreement with that to which we were led by a search for a natural mean (§ 2).

## § 8. SUMMARY, CONCLUSION AND ABSTRACT.

The atmospheric diffusivity in Fick's equation has been found by various investigators to increase from 0.2 to  $10^{11}$  cm.<sup>2</sup> sec.<sup>-1</sup> as the size of the cluster of diffusing particles increases from  $10^{-2}$  to  $10^8$  cm. The effect is due to eddies of many sizes acting together. There is apparently no way of modifying Fick's equation in order to describe this phenomenon. But a new mathematical method is here developed in which instead of thinking about concentration as a function of position, we think about  $q$ , the mean number of neighbours per length, as a function of  $l$ , their distance apart. Formal definition is given to this idea, and various properties of it are investigated. For simplicity only distributions on an unbounded straight line are considered, or projections of three-dimensional distributions on to the line. If the movement of concentration  $v$  is described by Fick's equation,

$$\frac{\partial v}{\partial t} + n \frac{\partial v}{\partial x} = K \frac{\partial^2 v}{\partial x^2}.$$

where  $t$  is time,  $x$  is distance,  $\bar{v}$  is mean velocity, and  $K$  is diffusivity. Then it is proved that

$$\frac{\partial q}{\partial t} = 2K \frac{\partial^2 q}{\partial l^2}.$$

If, however, the diffusion is "non-Fickian," as in the atmosphere, then the former of these equations cannot be generalised, but the latter can, taking the form

$$\frac{\partial q}{\partial t} = \frac{\partial}{\partial l} \left\{ F(l) \frac{\partial q}{\partial l} \right\}.$$

A discussion of existing observations shows that a rough average value is  $F(l) = 0.6 l^{4/3} \text{ cm.}^2 \text{ sec.}^{-1}$  for the atmosphere, when  $l$  lies between one metre and 10 km. The diffusion of a lamina is worked out from these principles. The diagram obtained in this way exhibits the size of a cluster because it is proved that the standard deviation of the  $(l, q)$  area from its centre  $l = 0$  is  $\sqrt{2}$  times the standard deviation of the cluster from its centroid.

Two methods are prepared for the observation of  $F(l)$  by balloons or smoke. Various allied topics are examined.

#### §9. LIST OF RECURRING SYMBOLS WITH THE SECTIONS WHERE THEY ARE DEFINED.

$K, \bar{u}, x, y, z, t$ , § 1.1;  $\Delta$ , § 1.2;  $[ ]$ , § 1.3;  $Q, h, N, A_{n,n+1}, l$ , § 3.2;  $v$ , § 4.2;  $q, v_1$ , § 4.3;  $\Pi$ , § 4.5;  $F(l)$ , § 5.1;  $\epsilon$ , § 5.2;  $\alpha$ , § 5.3;  $\beta$ , § 5.4;  $\sigma_m, \mu_n$ , § 6.8.

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*Condensation of Water from the Air upon Hygroscopic Crystals.*

By Dr. J. S. OWENS.

(Communicated by Sir Napier Shaw, F.R.S.—Received November 27, 1925.)

This paper describes experiments on the conditions of deliquescence of the crystalline salts found in dust records from the air, and has a bearing on the formation of haze, fog, and condensation from the air.

The possibility of identifying the nature of such salts when in very minute particles, so small that micro-chemical and crystallographic methods cannot be used, is indicated, the method being based upon the vapour pressure of deliquescence.

Arising from the experiments a method of examination of such crystals has been developed. Crystalline matter has been found in many dust records taken by the author with the jet-dust counter.\* Some consisting of practically nothing but crystalline matter were taken in the mouth of the St. Lawrence River, and others in Algarve in the south of Portugal. Having trapped the crystals, it appeared possible to develop a method for identification by examination of the conditions under which water commenced to condense upon them; hence the following experiments.

Before describing these it may be well to consider the conditions of deliquescence :—

A crystal of soluble salt will deliquesce when it is exposed to a vapour pressure equal to the vapour pressure of its saturated solution at the existing temperature. In fig. 1 are given a number of curves of vapour pressure for the saturated solutions of different salts and for water. If we assume that the temperature of the salt under observation is the same as that of the surrounding air, then when the salt is exposed to conditions of temperature and vapour pressure represented by the area to the left of and above the curve for that salt on fig. 1, deliquescence will take place, while if the salt is exposed to the conditions represented by the area to the right and below, the salt will remain dry, or if it has previously deliquesced, the water will evaporate, leaving a dry crystal.

When deliquescence of a pure salt has started, it will continue until all the salt is dissolved. Further condensation of water would then produce an unsaturated solution, the vapour pressure of which increases as the dilution increases. Condensation would continue until the solution formed had a vapour pressure equal to that of the surrounding atmosphere.

\* 'Roy. Soc. Proc.,' A, vol. 101, p. 18 (1922).

The theory of deliquescence of mixtures of salts has been examined by Prideaux\* for the case of considerable masses of the salts. It appears to be definitely accepted that when the saturated solution of a salt contains a small percentage of a second soluble salt, the vapour pressure is lower than if the second salt were not present. A mixture of salts when exposed to water vapour under suitable conditions will commence to collect liquid on the surface, beginning where particles of both are in contact, and thus forming at first a solution saturated with respect to both. As more water collects and the supply of one of the salts runs short, a solution is formed saturated with respect to one but unsaturated with respect to the other, and if the process is continued far enough for the whole of the mixture to be dissolved, a solution is formed containing the two salts in their original proportions. With such a solution there comes a time when equilibrium is established between the solution and the vapour pressure, due to dilution from the continued condensation of water.

Equilibrium may occur before the salts are completely dissolved if the surrounding vapour pressure is suitable—that is, if it lies between that of the solution formed at the moment when both salts are completely dissolved and that of the saturated solution of both. Thus there may be a partial deliquescence which ceases when a certain amount of liquid has collected and which is not continued until the surrounding vapour pressure rises.

Applying this to the suspended crystals in the air: if two crystals of different salts are attached or in contact, the foregoing process would seem to be inevitable. Tracing the history of a haze of such crystals as the vapour pressure and temperature vary, there may first be a partial deliquescence insufficient to dissolve all the salts, and equilibrium under such conditions; but this may be followed, if the vapour pressure rises, by further deliquescence, until the salt is completely dissolved and the vapour pressure in equilibrium with that of the new solution so formed. The rise of surrounding vapour pressure is met by increased dilution of the drops until equilibrium is established. If the suspended crystals are not in contact, deliquescence of each would occur under conditions determined by the vapour pressure of its own saturated solution, and under such conditions selective settlement may result.

#### *Method of Examination.*

The principle of the method adopted was to expose very minute crystals of the salt to the air and observe their behaviour under the microscope, at

\* 'Jour. Soc. Chem. Ind.,' vol. 39, p. 194 (1920).

the same time measuring the temperature and humidity by means of a wet-and-dry bulb thermometer or an Assmann psychrometer. The latter was used when the tests were made in a room where there was no breeze.

Tests were made with pure salts likely to be found in the air, mixtures of some of these, sea salt, and finally with crystals trapped on the dust records.

The method used for the pure salts, sea salt and mixtures was as follows :—

A microscope slide was prepared upon the surface of which a piece of thin card coated with shellac was cemented with bituminous cement. In this a number of circular holes were punched with a diameter of about 5 mm., forming a group of little cells. The glass floor of each was carefully cleaned until, when examined under the microscope with a dark ground illumination, it was free from smears and dust. An extremely small drop of solution of pure salt was placed in each cell on the point of a glass rod. The drops were next dried by heating and the slide placed face downwards upon a small open-ended wooden trough close to the end of an Assmann psychrometer. For each observation the slide was rapidly placed on the microscope stage, and all the salts could be observed very rapidly by moving it along. A good dark ground illumination was used, and each examination of the group of cells did not occupy more than half a minute. Thus there was little opportunity for changes in the temperature or humidity during the examination, while any change in the crystals during observation would have been evident. A 1-in. or  $\frac{3}{4}$ -in. objective was used, and the conditions of humidity were not changed artificially, but natural changes utilised. The illumination used was sometimes daylight and sometimes electric light, and in all tests care was taken not to breathe towards the salts, and only to approach them at intervals for the purpose of examination. Had there been any error introduced by the proximity of the observer, this would be noticed by a change during the actual observation; but no such change was seen, nor was there any change due to the heat from the electric light.

With the dark ground it was very easy to detect the first sign of water collecting upon any crystal.

The crystals from the air were treated differently. The cover glass, with its dust trace, was mounted face downwards on three pellets of wax upon a microscope slide, leaving a space of about 2 mm. between the cover glass and the slide for the air to get access to the crystals. Being very small they were observed under a  $\frac{1}{4}$ -in. objective, and the changes from solid to liquid were very easily noted.

When observing the behaviour of a very small crystal microscopically under gradually changing conditions of humidity, three stages may be observed :—

1. The crystal dry.
2. The corners rounding, liquid collecting, crystals dissolving.
3. Liquid only.      \*

State 2 is the one of interest at the moment, and if the crystal is sufficiently small and the conditions alter slowly enough, it must be very near the equilibrium condition ; while, if maintained for a time without any change occurring, state 2 would indicate the exact conditions for equilibrium. The errors which may occur in estimating the exact conditions for deliquescence are evidently reduced to a minimum if the crystals observed are small enough and the changes in humidity are made gradually.

There is evidence that after the crystal is completely dissolved and the liquid is subsequently evaporating, it reaches a condition of super-saturation before the crystal reappears, as when this process has been observed a crystal usually flashes into existence suddenly. It is therefore not safe to assume that, because the solution has no crystals in it, the vapour pressure is higher than that required for equilibrium with the saturated solution. It is best not to assume equilibrium unless both liquid and solid phases are present together for some little time.

The sensitiveness of the method is indicated by the rapid adjustment to the surrounding conditions observed. In one example deliquescence was caused by breathing on the record. All crystals immediately became liquid and drops present suddenly enlarged in diameter. In 4 or 5 seconds, however, all the drops had contracted to their original size, and the small crystals had re-formed in them. These crystals were about  $\frac{1}{2}$  micron wide by 3 microns long. In another case a crystal of sea salt 14 microns wide lay in a drop of liquid. The temperature was 58·5° F. ; vapour pressure, 7·4 mm. of mercury. On breathing upon this the crystal immediately disappeared, but reappeared again suddenly after 15 seconds.

#### *Pure Salts.*

In Table I are given, for each of the salts tested, the conditions at which the crystals were found to be "dry" or "wet." Calcium and magnesium chlorides and nitrates were liquid at all conditions within the range available.

All we can say from these figures is that the conditions for equilibrium lie



somewhere between the temperatures and vapour pressures corresponding with the dry and wet conditions.

Table I.

		Tempera- ture.	Vapour Pressure.	Relative Humidity.
		°F.	mm. Hg.	Per cent.
Sodium chloride.	Crystals dry .....	53·5	7·75	74
	„ wet .....	53·5	8·3	79
Ammonium chloride.	Crystals dry .....	56·5	7·9	68
	„ wet .....	50·5	8·0	86
Magnesium sulphate.	Crystals dry .....	60·0	9·4	71
	„ wet .....	62·3	12·2	85
Ammonia sulphate	Crystals dry .....	58·5	8·9	71
	„ wet .....	58·8	9·3	73
Sodium sulphate.	Crystals dry .....	58·5	8·9	71
	„ wet .....	58·5	9·3	73
Sodium nitrate.	Crystals dry .....	56·0	7·7	66
	„ wet .....	56·0	8·9	77·5
Ammonium nitrate.	Crystals dry .....	58·0	7·75	63
	„ wet .....	54·5	7·75	71

The curves given in fig. 1 of vapour pressure for the saturated solutions of different salts and for water are plotted from the published tables of different observers, whose names are given on the curves.

When we compare the conditions of deliquescence of crystals measured as described in this paper with these curves it will be seen that the points of deliquescence fall on the liquid sides of the equilibrium curves, thus supporting the theory that the vapour pressure of the saturated solution is the governing factor determining the conditions of deliquescence. The crystals of the salts observed were all very small—from 4 to 5 microns diameter to about 100 microns.

#### *Mixed Crystals.*

As the salts found in the air are unlikely to be pure, a very small crystal of sodium chloride and another of magnesium chloride were dissolved in water and the solutions mixed. A drop of the mixture was kept under observation, and very soon a group of well-formed cubic crystals appeared in the drop of liquid.

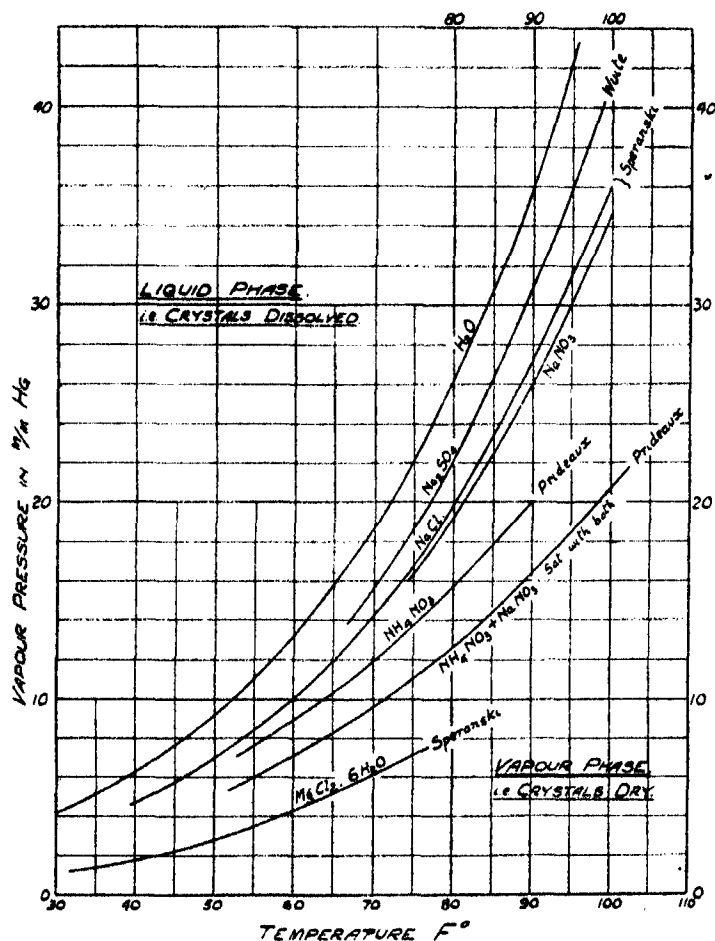


FIG. 1.—Vapour Pressure of Saturated Solutions.

Note.—NaCl curve below 75° F. is prolonged from Speranski's figures, assuming Babo's law of constant ratio to water.

The results were as follows :—

Temperature.	Vapour Pressure.	Relative Humidity.	Conditions.
°F.	mm. Hg.	Per cent.	
58	8.3	67.5	Group of cubic crystals, one 28 microns side in drop 70 microns diameter.
58.9	8.1	63	Several new crystals 4 to 5 microns side formed.
57.4	7.75	64	Small crystals re-dissolved.
53.5	7.75	74	Group of cubic crystals breaking up.
53	7.8	75	All crystals dissolved.

It is perhaps significant that in this test the crystals, evidently of sodium chloride, were clear and sharp most of the time, but the group began to break and dissolve at 53.5° F., vapour pressure 7.75 mm., a point practically upon the curve in fig. 1 for pure sodium chloride.

*Sea Salt.*

A sample of sea water from the Sussex coast near Rottingdean was tested in the same way. The sea water was evaporated, and a very small crystal kept under observation. There were small square crystals from 7 to 8 microns side and larger ones of 140 microns side.

In Table II are given the conditions when liquid and crystal were both present and no apparent change going on.

Table II.

Temperature.	Relative Humidity.	Vapour Pressure.
°F.	Per cent.	mm. Hg.
52.6	60	6.15
54.4	65	7.05
55.2	70	7.75
55.5	69	7.75
56.0	66	7.70
56.3	71	8.20
56.5	68	8.00
56.5	66	7.75
57.4	64	7.75
58.0	63	7.75
58.0	67.5	8.30
58.5	71	8.85
59.0	65	8.32
60.0	71	9.38
63.5	70	10.50
64.6	68	10.42
66.0	67	10.90

A curve has been plotted from these figures (fig. 2), and it will be seen that the points are somewhat scattered, as would be expected with an impure salt, since the conditions for equilibrium might be different as different proportions of the salts present were dissolved. The curve also bends away from the water curve in a curious way.

It is interesting to compare the conditions of equilibrium for the sea salt with those of crystals found in a record taken on the foreshore at the same time as the sample of sea water. This will be referred to later.

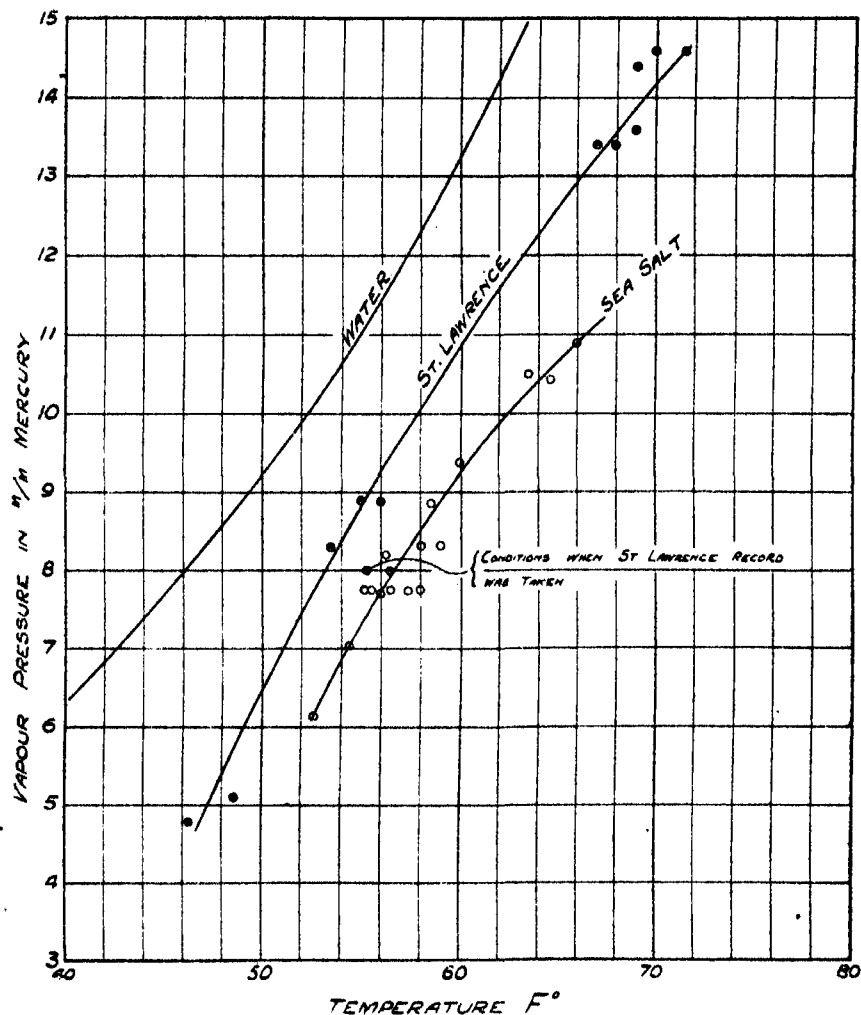


FIG. 2.—Equilibrium Curves of Crystals.

#### Crystals from the Air.

*Portuguese Record.*—The author obtained records in April, 1922, in Algarve in the south of Portugal, which contained practically nothing but crystalline matter. They were taken during a bright sunny day near the coast, and there was a definite blue haze. In April, 1925, he again obtained in the same place almost similar records, the crystals being mostly square and tabular. One of the latter records was kept under observation as above described, with the results shown in Table III.

There was evidence of mixed salts here as the crystals did not all deliquesce

under the same conditions, nor were they all the same shape. It is clear, however, that condensation would commence upon these salts long before the air had become saturated in the ordinary sense. For example, at a temperature  $56^{\circ}\text{F}$ ., vapour pressure  $7.9\text{ mm.}$ , relative humidity 69 per cent., the crystals began to collect water. This point falls just below the curve for pure  $\text{NaCl}$  (fig. 1) and suggests  $\text{NaCl}$  with some impurity. Again, all crystals were dissolved at a temperature of  $58.5^{\circ}\text{F}$ ., vapour pressure,  $8.8\text{ mm.}$ , relative humidity 70 per cent., a condition when it is evident a fog of liquid drops might be formed from these crystals.

*St. Lawrence Record.*—On July 31, 1924, during bright sunshine and a strong westerly wind there was a white haze over the water at the mouth of the St. Lawrence River. Records obtained by the author from the bow of s.s. "Caronia" were almost entirely crystalline. At the time the dry bulb was

Table III.—Crystals from Haze in Algarve, Portugal.

Crystals in field :—(1) A rectangular plate  $3 \times 2$  microns, with needle-shaped crystal passing through axis. (2) A group of tabular crystals with one needle-shaped crystal  $7\frac{1}{2} \times 1$  micron. (3) An irregular plate  $3 \times 3$  microns. (4) An irregular plate  $3 \times 4$  microns. (5) A small nearly circular crystal 1 micron diameter.

Time. B.S.T.	Dry Bulb.	Wet Bulb.	Relative Humidity.	Vapour Pressure.	Condition of Crystals.
1925.	$^{\circ}\text{F.}$	$^{\circ}\text{F.}$	Per cent.	mm. Hg.	
June 2					
12.20 pm.	63	53.5	50	7.3	No sign of condensation.
10.25 "	57.5	51.2	62	7.8	No certain change.
11.10 "	56	51	69	7.9	All large crystals dissolving in drops.
June 3					
7.25 a.m.	62	55	61	8.7	All crystals gone except needle and one or two others. Many drops had needle-shaped crystals forming or not entirely dissolved. Signs of skeletal crystals.
8.5 a.m.	61.5	55.5	67	9.2	All drops show signs of crystallisation. Needles in No. 1 still intact. Salts of different kinds present. Rectangular crystal formed.
8.45 "	64.5	57	61	9.4	Crystals more marked, but mostly liquid.
6.15 p.m.	68	58	51	9.0	All crystals re-formed and dry.
6.45 "					Breathing gently near record caused all crystals to become drops.
7.15 "	66	56	50	8.2	Drops still remain, crystals re-forming.
7.55 "	64	56	58	8.9	No change.
8.40 "	61	55	66	9.1	No certain change, crystals in drops a little less well defined.
9.10 "	59	54	70	9.0	Crystals getting less clear of outline, but still there.
9.45 "	58.5	53.5	70	8.8	Crystals all gone, dissolved in drops.
June 4					
7.40 a.m.	65	57	59	9.2	Crystals all re-formed, liquid gone.

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55.3° F., the wet 50.8° F., indicating a relative humidity of 71 and vapour pressure, 8 mm. The crystals were mostly skeletal, many needle-shaped and in masses of about 6 to 8 microns diameter; the needle or rod-shaped crystals were about 0.5 micron thick by 3 microns long.

Selecting conditions when both liquid and crystal were present enough points were obtained to plot the curve in fig. 2. These points are given in Table IV.

Table IV.

Temperature.	Relative Humidity.	Vapour Pressure.
° F.	Per cent.	mm. Hg.
46.3	58	4.8
48.6	59	5.1
53.5	70	8.3
55	80.5	8.9
56	77.5	8.9
67	79	13.4
68	77	13.4
69	75	13.6
70	77	14.6
71.5	73	14.6

Referring to the figure, the conditions when the record was taken are shown by the full black dot, and the position of this, on the vapour side of the curve, suggests that the haze consisted of dry crystalline matter rather than of liquid drops. It is evident, however, that a very slight increase of humidity would have made the haze into a fog of liquid drops. Here again it is clear that condensation will begin at humidities far below saturation. It will be seen that the curve bends away from the water curve in the same way as that for sea salt and differs from those for the equilibrium of saturated solutions. The explanation of this is not evident unless it be due to increased solubility of the salts present with rise of temperature.

On breathing gently towards the record while on the stage of the microscope all crystals immediately became liquid and the drops which covered the field enlarged suddenly in diameter. In four or five seconds the drops had contracted to their original size and the crystals had re-formed. This experiment was repeated several times with the same result. The crystals were needle-shaped and a few were skeletal in form. As already mentioned, this indicates the sensitiveness to surrounding conditions and also suggests the presence of more than one salt. It may be noted that the conditions when the experiment was made, temperature 71.5° F., vapour pressure 14.6 mm., fall just below the NaCl curve (fig. 1).

*Cheam Crystals.*

On June 6, 1925, during a bright sunny morning with a gentle easterly wind, a thick haze was carried to the south-west of London. At Cheam the haze was well marked and a dust record was taken at 8.50 a.m. from 1000 c.c. of air, the damping chamber of the dust counter being slightly warmed. In using the jet dust counter the air is drawn in through a chamber lined with wet blotting paper, and if this be held in the hand to warm it slightly, it causes an excessive deposit of water on the dust record which washes out soluble salts. The water is blown out sideways by the air current deflected when it strikes the cover glass and thus forms streams, which usually evaporate, leaving dried beds where crystals are likely to be formed.

This record contained a large number of dust particles, while from the sides of the dust trace there were dried-up stream beds where the excess water had been blown out laterally. The ends of these stream beds were full of crystals, not well formed but very plentiful. There were some rhomboidal crystals in the stream beds and they were very numerous in the dust trace. These rhomboids varied in size, the largest being about 3 by 6 microns, and so numerous that under a  $\frac{1}{8}$ -inch objective there were 15 to 20 in the field at once. This record was placed in a breeze and a wet-and-dry bulb thermometer near it read at intervals. Some of the crystals at the heads of the stream beds deliquesced at 62° F., vapour pressure 11 mm., relative humidity 77 per cent., but not the rhomboids. The crystals dried again at 75° F., vapour pressure, 12.5 mm., relative humidity 57 per cent., and they subsequently collected water again at 64° F., vapour pressure 11.1 mm., relative humidity 73 per cent. There were clearly different salts present with different degrees of affinity for water. Some would have produced a fog of liquid drops, under the conditions of humidity mentioned, at 64° F., while the rhomboids did not deliquesce within the range tested and would not therefore be so effective in initiating condensation. If the point corresponding to 62° F. and 11 mm. be plotted on fig. 1, it will be seen to fall between the prolongation of the curve for  $\text{Na}_2\text{SO}_4$  and that for  $\text{NaCl}$ . The rhomboids could not have been any salt shown in fig. 1. The presence of sulphates and chlorides is highly probable, as the haze drifted from London.

Here, again, the presence of liquid and crystals in apparent equilibrium with the surrounding vapour was observed, evidently due to mixed salts.

On September 13, 1925, there was a white fog at Cheam, which cleared at 10 a.m., leaving a thick haze; the wind was light between north and east. A dust record from 200 c.c. of air was taken, which contained a large number of round particles from about 1 micron down, and a few larger,

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apparently crystalline. This was mounted record up upon a slide and kept under observation, and it was noted that when the air outside was clear of fog the crystals were dry, but that as the fog came on later the crystals became liquid, subsequently drying again when the fog cleared a second time. This indicates that the points of deliquescence obtained as described are probably the same as when the crystals are suspended in the air.

### *Rottingdean Crystals.*

A dust record from 500 c.c. of air was taken when the sample of sea water referred to previously was obtained, and the record contained numbers of crystals, mostly spindle-shaped and about 9 microns long by 1 micron diameter. When breathed upon, these crystals deliquesced and re-crystallised in a skeletal form. They were found to be dry at 48.6° F., vapour pressure 5.1 mm., relative humidity 59 per cent., and liquid at 44.5° F., vapour pressure 5.7 mm., relative humidity 77 per cent. It is curious that under both these conditions the sea salt crystals were dry. The liquid condition falls on the NaCl curve in fig. 1.

### *Bournemouth Crystals.*

A dust record from Bournemouth taken in August, 1925, contained crystals similar in appearance to those obtained at Rottingdean, and these were in approximate equilibrium with the surroundings under the following conditions :—

Temperature.	Relative Humidity.	Vapour Pressure.
° F.	Per cent.	mm. Hg.
64.5	66	10.2
61.9	67	9.4
58.5	71	8.9
56.3	71	8.2

These points fall a little below the NaCl curve (fig. 1), indicating a somewhat more hygroscopic salt, or mixture, than pure NaCl.

### *General Inferences.*

A comparison of the conditions for deliquescence with the equilibrium curves of saturated solutions gives a possible means of identifying the salts. It is complicated, however, by the fact that the salts found in the air are not



likely to be pure ; still, there is some indication of a tendency for the crystals of different salts to remain separate on dust records, and if isolated crystals be examined, the error from impurity may not be very great.

The conditions under which haze becomes converted into a fog of liquid drops can be found by observation of the crystals obtained in dust records from that particular haze. The fact that such crystals are probably impure salts suggests that they might be in equilibrium with their surroundings through a certain limited range of conditions, so that when condensation began on such crystals it could not be inferred that if the conditions remained constant it would continue. A fog might also persist owing to supersaturation at a temperature and relative humidity corresponding to the solid phase for the salts present. In other words, it may be easier to produce a fog than to dissipate it when formed. It may also be inferred that the conditions which will cause condensation to begin upon such crystals will fail to do so upon insoluble dust.

It can hardly be expected that the exact salt present would be indicated with certainty by the methods described, but certain salts can be excluded with certainty and a smaller group left to select from ; with some guidance from surroundings as to the possible salts, the indication given is sufficiently clear.

It has been noted by different observers that sodium chloride is easily detected in the air and rain near the sea coast.\* Crystals have often been obtained by the author on the sea and in its neighbourhood, but rarely far inland. A probable explanation for this is to be found in the behaviour of such crystals when the air cools down at night ; if the vapour pressure is then suitable, as it usually is, they will collect water, increase their mass, and the drops so formed would probably settle comparatively rapidly in still air.

As different salts deliquesce under different conditions, it is reasonable to expect that as the temperature falls at night there will be a selective deposit commencing with the most hygroscopic salts, so that it does not appear safe to assume, as is sometimes done,† that crystalline matter found in the air and originally derived from the sea has the identical composition of sea salt.

#### *Another Method of Examination.*

In the method described it is not easy to control the temperature and vapour pressure, and therefore a considerable time is spent waiting for changes in

\* *Vide* Wilfrid Irwin, 'Meteorological Magazine,' April, 1925.

† Hilding Kohler, "The Condensation of Vapour in the Atmosphere," 'Geophysical Publications,' vol. 2. Danish Geophysical Commission, 1921.

these. There is also the need for obtaining equilibrium curves of vapour pressure for all the salts likely to be present. A second method was therefore devised which, although not thoroughly tried out yet, promises greater accuracy with less expenditure of time. This is to expose the crystals in a small air-tight cell to the vapour of the saturated solution of pure salts. It is found that when a crystal is so enclosed and the vapour pressure is higher than its own saturated solution, it deliquesces, and when lower it remains dry. It also deliquesces in the vapour of a saturated solution of the same salt, although it should apparently be in equilibrium. The fact that it does so deliquesce has been established by a number of tests made with great care. Possibly small variations of temperature between the dry crystal and the solution initiate condensation on the crystal.

Minute crystals of sodium chloride enclosed with a little pure water in a small cell rapidly deliquesced, but when a saturated solution of magnesium chloride was placed in the cell, the sodium chloride crystals which were lying in drops rapidly dried.

A very pretty experiment was tried as follows :—A microscope slide with a hollow ground in the surface had a cover glass sealed over the hollow with a little vaseline and upon the inside of the cover glass were placed two drops, one of saturated NaCl, the other of water. The drops were approximately the same size, the salt solution was 1.13 mm., the water 0.87 mm. in diameter where in contact with the glass ; they were about 4 mm. apart. In 20 minutes the salt drop had grown to 1.45 mm. diameter, the water had disappeared. The temperature at the time was 57° F. and the illumination used daylight.

Next a drop of a saturated solution of  $MgCl_2$  and another of NaCl were put on the cover glass about 4 mm. apart. Both drops measured 1.1 mm. diameter where in contact with the glass and the contact was practically circular. The NaCl drop immediately developed crystals, which were formed chiefly at the glass surface, and these were seen continually falling away from the glass and sliding down the inside surface of the drop to collect in a heap at the lowest part, the surface film of the inverted drop acting as a pouch. They were beautifully formed cubes and rectangular tablets. The crystals continued forming and dropping down until, later on, by shrinkage of the drop, they were pulled up into contact with the glass and the water disappeared, leaving them dry. Meanwhile the  $MgCl_2$  drop had grown to 1.35 mm. diameter. This happened in about 1½ hours. The temperature was 58° F.

To try if the glass surface in contact with the crystals had any effect in promoting deliquescence, a cover glass had one-half coated with a thin film of

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paraffin wax. Upon the plain and coated parts very small drops of NaCl solution were placed and allowed to evaporate, leaving minute dry crystals. The cover glass was sealed with vaseline over the hollow in the slide, as above described, while in the bottom of the hollow was placed a drop of saturated solution of NaCl. In four minutes the dry crystals on the plain and waxed parts showed some water round them. After two hours all crystals were lying in pools of water, the same on both parts of the glass. To make sure that the drop of solution enclosed with the crystals was saturated, it was watched under the microscope, before enclosing, until numbers of crystals began to form.

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**OBITUARY NOTICES**  
**OF**  
**FELLOWS DECEASED.**

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*Rudolph Messel*

# RUDOLPH MESSEL—JANUARY, 1848, TO APRIL, 1920.

RUDOLPH MESSEL was the son of Simon Messel, a banker of Darmstadt. He was the second of five children, of whom four were to make their homes in England; the fifth acquired great distinction as an architect in Berlin. He lost his father when 11, and shortly after was sent to a Huguenot school at Friedrichsdorf in the Taunus, where he remained until he was 15 years old. His schoolmaster, Philip Reis, was the inventor of the first telephone. Messel, in his Presidential Address to the Society of Chemical Industry in New York in 1912, makes reference to the fact that he "assisted Reis in making the mechanical parts of some of his instruments and also repeatedly in his experiments, Reis being at one end of the circuit, speaking or singing, I listening at the other, or *vice versa*." About this time the family circumstances changed, and it was clear that Messel would have to become self-supporting at an early date. It was his intention to become an engineer, and in 1863, he discussed his further course of action with an old friend of his father's, H. Rau, then living in Frankfort. Rau appears to have advised Messel to devote himself to the study of commerce which he said would rapidly lead to independence, and to combine with this the study of Chemistry, Physics and Technology, and so become a manufacturer. It is clear that Messel's whole course of action was influenced by this letter, as not only did he keep it to the last among his rarest letters, but followed the advice it contained almost verbally.

In April, 1863, he became apprenticed to E. Lucius in his wholesale drug and chemical factory in Frankfort, and remained there until September, 1866, leaving to enter the Federal Polytechnic in Zurich, where he followed the regular first-year course. The following winter he spent at Heidelberg, studying physical chemistry under Erlenmeyer. He moved in the spring to Tübingen, where he finished his education, studying chemistry under Strecker, and continuing with him until April, 1870, carrying out work for which he obtained his degree. In April, 1870, he came to Manchester, originally to act as private assistant to Roscoe.

He was recalled to Germany owing to the outbreak of the Franco-Prussian war, where he served as a stretcher-bearer in the army of the Loire and was wounded. When recovered, he returned to England, where he remained during the rest of his life and ultimately became an Englishman.

He entered the service of Messrs. Dunn, Squire & Co., Stratford, as assistant to Dr. Squire. Shortly after, Squire formed with Spencer Chapman the firm of Squire, Chapman & Co., and took Messel with him in his new venture. This change occurred at a time when the growth of the synthetic dyestuff industry was threatened by the excessive price which was charged for fuming



sulphuric acid, then produced by the old Nordhausen process in Bohemia. Squire decided to commence the manufacture of fuming acid.

In his New York Presidential Address, Messel tells of a conversation in the beginning of the '70's with his former teacher Strecker, and Brüning of Höchst, on the importance of fuming sulphuric acid in the synthetic alizarin industry. To his question how the acid should best be made, Strecker gave the reply: "That is a problem for you to solve." A few experiments convinced him, he says, that, given pure gases, the catalytic action of platinum was the rational solution of the problem. In April, 1875, a telegram came to him at the laboratory from Squire, asking him to read up that night about Nordhausen acid, as it was wanted by an Alizarin Works. The response was immediate and typical—no reading was necessary. Next day he showed how simple a matter it was to unite sulphur dioxide with oxygen by means of platinum. However, Squire was conventional and thought that the decomposition of acid sulphate would be a simpler method. Experiments were made, as requested, but eventually Messel was told to try his dodge.

Of the work that followed, no permanent record has been published, except in the form of Patents taken out by Squire in 1875. A year later, however, in April, 1876, Squire and Messel described and demonstrated the process before the Chemical Society. This paper was never printed, probably because of the Patent situation, but a paragraph in the 'Chemical News' records the meeting. Messel treasured until his last days a document describing the experiments, and the original platinum apparatus used was left by him in his will to his lifelong friend, Professor H. E. Armstrong.

In his Presidential Address, Messel refers to the publication in October, 1875, by Winkler, of a process which was practically identical with his. Both investigators erred at that time in believing that stoichiometrical proportions of the gases were the best to use, and the various similarities gave rise to unpleasant comment. In letters to Messel, however, Winkler freely acknowledges the independence of Messel's work, and only regrets that he had deprived himself of the benefit of the invention by his publication.

The process was established at Silvertown, and in 1878 Messel succeeded Squire as manager of the works, which he only quitted in 1915, when his health gave way under the excessive strain of the times. The firm became Spencer, Chapman & Messel, Ltd., and the factory grew in size and importance.

Messel remained a bachelor and lived on the works. He was an indefatigable worker, and set a very high standard to all those who served under him. His sense of justice and sympathy, and the fact that he lived amongst them, gave him great popularity and power with his workpeople.

In the early days of the industry, the value of the fuming acid was much greater than that of oil of vitriol and the most suitable mixture of sulphur dioxide with oxygen was made by decomposing the latter. As experience was gained,

and the difficulty of condensing the anhydride was overcome, sulphur dioxide prepared by burning sulphur and ordinary air were used, and later, excess of air was employed largely as a result of observation by the foreman that the plant worked better under these conditions.

It is a testimony to Messel's remarkable insight that right at the beginning he obtained such a wonderful knowledge of all details of this catalytic process, subsequently developed on a very large scale and in great detail by Dr. Kneitsch and his co-workers of the Badische Anilin und Soda Fabrik.

Remarkable as Messel was as an industrialist, he was even more remarkable as a man. A man of astounding vigour and feeling, he had little thought for himself and a hatred of all display. He was essentially an artist, both in his extreme devotion to his own art of chemistry and in his love of the company of artists and other bohemians. He was everything—not only chemist, engineer and business man, but also took care to cultivate the social side of his life, and was almost the only manufacturer of his day who attended regularly at scientific gatherings and showed a real interest in the proceedings. His vigorous frame, black hair and sparkling eyes, his smiling face and peculiar guttural accent will remain in the memory of all who knew him. He never mastered English properly though he spoke it fluently. He was very fond of young people, many of whom rejoiced in his generosity. One of the most lovable of men, his outlook on life was always cheerful and optimistic. The example he set in leaving his fortune to science is a remarkable one and best proof of his considerate outlook. Honest and sincere himself, he hated insincerity and all meanness of spirit.

He played an active part in many scientific societies, particularly the Society of Chemical Industry, of which he was Foreign Secretary for many years and President for 1911-1912—probably the only connection in which he showed vanity, but he was very proud also of his election to the Royal Society in 1912.

His Presidential Address was written to show that science and industry are working hand in hand, and the importance of the results that such co-operation has produced. In discussing the education of a chemist, he stressed the fact that too early concentration on special subjects had a bad effect on the development of the power and habit of thinking independently and on the faculty of imagination in the student. He held that technique is very rapidly acquired in practice by one who has been scientifically trained. With Carlyle he said, "He who has learned how to learn can learn anything," and the best system of education is the system which teaches each man how to educate himself. Gifted with his full share of enjoyment of the good things of this life, Messel nevertheless led a life of great simplicity. His success was due, in the first place, to his thorough scientific training and scientific outlook, but in an exceptional degree to his moral attitude towards his work.

He left four-fifths of his residuary estate to the Society and the remainder to the Society of Chemical Industry. Without imposing any trust or obligation, he desired that the capital should be kept intact and the income applied to the furtherance of scientific research and other scientific objects.

E.F.A.

FREDERICK THOMAS TROUTON—1863–1922.

FREDERICK THOMAS TROUTON was born in Dublin on the 24th November, 1863, being the youngest son of Thomas Trouton of that city. He was educated at Dungannon Royal School and at Trinity College, Dublin. He graduated M.A. and D.Sc. (Dublin), and received a large Gold Medal in his year. He was appointed Assistant to Prof. G. F. FitzGerald in 1884, and became Lecturer in Experimental Physics in 1901—a post which he held for two Sessions. In 1897 he was elected a Fellow of the Royal Society.

In 1902 he was appointed Quain Professor of Physics, London, and held this post until 1914, when serious illness compelled him to relinquish it. He lived in retirement at Tilford in Surrey, and afterwards at Downe in Kent, until 1922, when, on September 21st, he passed away in the 59th year of his age. He kept his mental faculties little impaired until his death, although paralysis of the lower limbs had taken away all power of locomotion during the last five years of his life.

In 1887 he married Annie, the daughter of George Fowler, of Liverpool, and through her had four sons and three daughters. His two eldest sons were killed in War service; of these the eldest, Eric, was a promising student of Physics at Trinity College, Cambridge; the other, Desmond, a keen Engineering student at University College, London. His wife and the remainder of his children survive him.

While still a student Trouton pointed out a relation between the molecular latent heats and boiling points of various substances, which is known to every physical chemist as Trouton's law ('Phil. Mag.,' vol. 18). He himself was disposed to depreciate the discovery of this law, regarding it as the result of an afternoon's manipulation of figures. But the law plays an important part in many physico-chemical discussions, and, though criticism has shown that it cannot claim to be exact, it is at least a useful rule. The rule is equivalent to saying that the change of entropy per molecule in evaporation at its boiling point is approximately the same for various substances.



*Fred G. York -*



Later on he came back to the subject of latent heats and published experimental investigations on the latent heat of evaporation of steam from saturated salt solutions ('*Trans. R. Irish Acad.*,' vol. 31, p. 345, 1900) in which he obtained satisfactory agreement between the experimental values and values calculated by means of a thermodynamic cycle.

Much of his earlier work was inspired by Prof. G. F. FitzGerald. In 1886 was begun an investigation to test the accuracy of Ohm's law for electrolytes. The method employed is that carried out for metallic conductors by Maxwell and Chrystal. A Wheatstone's bridge was employed in which two of the arms were of about equal sections and resistance, while the remaining two, though equal in resistance to one another, have sections very different from the first pair. If Ohm's law were not true the point of balance would vary with the amount of current passing through the combination. To avoid complications arising from the unequal disturbance of the resistances by the heat developed a rapid alternation of a large and small current was employed. A balance obtained in this case could only be an average one if Ohm's law were not true, in which case, on reversing the direction of one of the currents, the two which previously cancelled each other would now conspire to produce a deflection. Copper sulphate solution was the electrolyte employed. The inequality between the unequal arms was very considerable; one was 119 cm. long by 2.38 cm. internal diameter, whereas the other was a hole drilled in very thin mica and 0.0027 cm. diameter. As a final result of experiments extending over several years ('*Brit. Assoc. Reports*,' 1886, 1887, 1888) it was decided that in the formula  $R = R_0(1 - hC^2)$ , where  $C$  is the current,  $h$  is not greater than  $3 \times 10^{-6}$ . For metals, Chrystal had shown that  $h$  is less than  $10^{-12}$ . An item of historic interest is that "they hoped soon to have storage cells in the laboratory," in connection with the driving of the intermitter.

FitzGerald was one of the few physicists who took Maxwell's electromagnetic theory of light seriously. Consequently it was to be expected that when Hertz began publishing his investigations on electric waves, FitzGerald should be one of the first to give a detailed account of them (*Brit. Assoc.*, 1888, Bath meeting), and to stimulate the Dublin laboratory to extend and interpret them. Trouton was his co-worker in studying cases of reflection from non-conducting substances such as glass and paraffin. They also decided the question of the relation of the azimuth of vibration to that of polarisation. In one sense the answer is twofold, because in the electromagnetic wave there is both an electric and a magnetic vibration. Trouton's experiments on reflection at the polarising angle from the surface of a bad conductor proved that when the electric vector is in the plane of incidence the reflection is bad, but reflection occurs at all angles when the electric vector is at right angles to that plane. He also showed that a small reflector, i.e., one approximately

like the pole of a wave, reflects a wave nearly a quarter of a period in advance of the whole reflected wave, and thereby justified experimentally the somewhat puzzling introduction of a "quarter-wave advance" by Stokes in connection with Fresnel's treatment of a primary wave as the resultant of effects arising from elementary wavelets or secondary waves.

A series of papers on the relative motion of the earth and æther forms another indication of FitzGerald's influence. The fundamental idea of the first experiments is that a charged condenser, when moving through the æther with its plates parallel to the direction of motion, possesses magnetic energy as well as electrostatic, in accordance with the generally held view that a moving charge is equivalent to a current-element. FitzGerald's view as to the source of this energy was that it would be found as being due to a mechanical drag on the condenser itself during the process of charging. Trouton arranged an experiment to test this conclusion. Initial experiments were in progress, and were apparently leading to a negative result, when FitzGerald died, but Trouton records that FitzGerald, in conversation with him, had expressed the view that the negative results, if sustained by further work, would be attributable to the same cause as the negative results in the Michelson and Morley's experiment, viz., an alteration in linear dimensions of the moving system according to the direction of motion in the æther. From some such cause a diminution in the electrostatic energy might be brought about, when the condenser was in the edge-wise position, just sufficient in amount to provide for the energy required for the magnetic field. Further consideration of the problem convinced Trouton that it was a turning-impulse and not a translational one that was to be expected. The extra energy gained in turning the condenser through ninety degrees would then come from the work required to effect the rotation. In any intermediate position a couple would be experienced which would have a maximum value in the 45-degree position. Assuming a positive result to be obtained Trouton pictured the possibility of building a machine consisting of air-condensers for utilizing the vast store of energy in the Earth's motion through space. Experiments on this turning-moment were not carried out until after Trouton's appointment to University College, London, when, in conjunction with a research student, Mr. H. R. Noble, a very complete experimental investigation was made. A mica condenser with its plane vertical was suspended by a fine wire. The charges were let into the plates of the condenser by means of this wire and by a wire which hung from beneath and dipped into a liquid terminal. Observations were taken at different times of the day, when the plane of the condenser made various angles with the direction of the drift. Calculations had been previously worked out as to the best time of day on different days at which the effects sought for might be a maximum, taking account of the earth's motion round the sun and the motion of the whole solar system in space. The condenser was set in oscillation and a series of

elongations taken alternately with the condenser uncharged and charged. From the elongations the equilibrium positions in the two cases were calculated. After many months' experience with the apparatus, the *largest* displacement of the equilibrium position was barely 5 per cent. of the value calculated from theory. These small displacements were attributed to perturbation of the surrounding air arising from small sparks taking place inside or over the condenser. The final conclusion was that the electrostatic energy must diminish by a fraction  $(u/V)^2$  of itself when moving with a velocity  $u$  at right angles to the electrostatic lines of force.

Assuming that FitzGerald was right in his contraction hypothesis, Trouton was led to seek for more positive evidence of its truth. Amongst the physical properties which might be modified by the contraction there is the electrical resistance of a wire. The dependence of the resistance on the specific resistance ( $\rho$ ) length ( $l$ ) and cross-sectional area ( $a$ ) implies the relation

$$\frac{dR}{R} = \frac{d\rho}{\rho} + \frac{dl}{l} - \frac{da}{a}.$$

If  $\beta$  is written for  $u/V$ , turning a wire through a right angle might be expected to produce a change given by

$$\frac{dR}{R} = \frac{d\rho}{\rho} + \beta^2,$$

where  $\beta^2$  is the term arising from change of dimensions. The investigation was carried out in conjunction with Mr. A. O. Rankine (now the Director of the Optical Department in the Imperial College, London). Four rectangular coils were wound, mounted on a common stand and connected in such a way that they formed a Wheatstone network such that the wires forming opposite arms of the bridge were parallel. The whole could be rotated bodily on an axis. Balance was obtained when the wire in two of the coils was at right angles to the resultant drift. The whole was turned through 90 degrees and the change of balance tested. The usual difficulties arising from variable temperatures and thermo-electric currents were met with. The outcome of the determinations made with every realizable precaution was that for the two positions a mean difference of scale-reading of only 0.13 mm. was observed, whereas for the value of the drift on the particular day on which the experiments were made, the expected value from  $\beta^2$  alone would be 10.9 mm. The final conclusions are stated by saying, firstly, that the total electric resistance of a wire is not altered by an amount exceeding  $5 \times 10^{-10}$  of its value by any change of its position relative to its motion through space; and secondly, that if the FitzGerald shrinkage takes place the specific resistance of a material must also be dependent upon the direction of the current, being greater to a current flowing parallel to the velocity of the material through space than to a current in a perpendicular



direction. Such a change of specific resistance can quite plausibly be deduced from electronic theory as arising from the change of dimensions.

These experiments, in each case leading to a negative result, helped to demonstrate the illusive nature of the luminiferous æther and to pave the way for the various theories of relativity which dominate the situation at the present time.

For some years the problem of the viscosity of quasi-solids attracted his attention, and much ingenuity was displayed in investigating it. In conjunction with Mr. E. S. Andrews he applied the bending beam method to pitch (viscosity,  $10^{11}$  C.G.S. units). By a torsion method they obtained the viscosity of soda-glass at different temperatures, and even the value for shoemakers' wax ( $4.7 \times 10^6$  C.G.S.). Stokes' method of a falling sphere was applied to the last material, the velocity of a bicycle ball falling through it being obtained by observing the shadow of the ball when X-rays passed through the wax and fell on a fluorescent screen. The ball took a fortnight to travel 1.8 cm. This method for the examination of opaque media was originated by Trouton, but has been reintroduced in recent years by others with a similar object.

While at Dublin researches were begun on the adsorption of water vapour by flannel, glass and other substances, the immediate object in view being, if possible, to construct a recording hygrometer based either upon the change of weight or, in the case of glass, the change of electrical resistance between two wires fused on to the surface. Though the immediate aim was not successful, these investigations led up to a long series of others on adsorption. In the course of these experiments several curious effects were observed (in collaboration with Mr. J. H. C. Searle) when voltages were applied between electrodes mounted on glass. It was found possible for the resistance to be of the order  $2 \times 10^6$  ohms, while for a voltage applied in the reverse direction it was  $10^8$  ohms. The effect was observed to be very sensitive to changes in the hygrometric state of the atmosphere, as well as on the length of time the current was allowed to run before reversal. In further study of the deposit of moisture on glass—a study which was carried out with the most scrupulous care—it was found that if the amount of water admitted to a vessel which was filled with glass wool was gradually increased, the equilibrium pressure of the vapour varied continuously, but the curve obtained by plotting pressure against water-content had a marked kink in it, analogous to the kink given by Van der Waals' equation for gases. A curious consequence is that it could be arranged for a glass surface holding a certain amount of water to have a less vapour pressure than a drier surface. Analogous effects were observed with phosphoric pentoxide. If *very* dry and ordinary phosphoric pentoxide are placed side by side under a bell jar and water be admitted in small quantities day by day, the ordinary oxide gets continually wetter, while the dry remains dry (except for a few specks probably due to dust or other impurity)—it is, in fact, too dry to take up moisture at all.

At the time when he first fell ill work was being conducted on the general

phenomena of adsorption with the help of his assistant, Mr. Burgess, to whose accuracy and care Trouton readily bore witness. It was made clear that the effects observed with glass and water vapour were not peculiar to them, for similar effects were obtained with the adsorption by silica of the salt from various salt solutions. These researches have not been published in detail, but a brief account is given in Trouton's Presidential Address at the Australian Meeting of the British Association (1914)—an address which he was unfortunately not able to read in person, as he was even then too ill to undertake the journey.

As an example in a lighter vein, attention may be called to a letter in *Nature* (December 14, 1893) jointly with FitzGerald on "Systematic Nomenclature." Following the example of "resistance" and "resistivity," it was suggested to introduce terms like "diffusance" and "diffusivity," "emissance" and "emissivity," "expansance" and "expansivity," "frictance" and "frictivity," etc., etc. Although these suggestions were treated perfectly seriously, the writer has Trouton's own statement that it was in an atmosphere of rather hilarious levity that the letter was concocted.

Owing to his long severance from active life through illness, Trouton is known personally only to a minority of the younger generation. Those who had the advantage of personal acquaintance with him remember him for his integrity, for his lively imagination, touched often with characteristic Irish whimsicality, for his friendliness and helpfulness. He cared little for the ordinary attractions of a town. It was a delight to see him in his country home, where he could indulge in his love for gardening and other outdoor pursuits. He took a keen interest in the athletic life of the College. His scientific friends will remember him in particular for his insight into the provisional character of all scientific theories and for his recognition of the importance of experimental research.

A. W. P.

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## JOHN VENN—1834–1923.

JOHN VENN, M.A., Sc.D., F.R.S., F.S.A., logician and antiquary was born August 4, 1834, and died April 4, 1923.

No one could have had a more uncompromisingly clerical ancestry and upbringing than had Venn. His five or six immediate ancestors, whose lives he gave in his notable book "The Annals of a Clerical Family," were vicars or rectors occupying positions of importance in the Church.

His own upbringing was in the narrowest atmosphere of Low Church Evangelicalism, and, owing to this, he came to the University with so slight an acquaintance with books of any kind that he may be said to have begun there his knowledge of literature.

Venn entered Gonville and Caius College from Islington Proprietary School in 1853, and was sixth wrangler in the Mathematical Tripos of 1857—a time when a man's position in the list depended greatly upon the coach with whom he had read. He was elected Fellow of his college in the same year, took Priest's Orders in 1859, and was for a year curate at Mortlake.

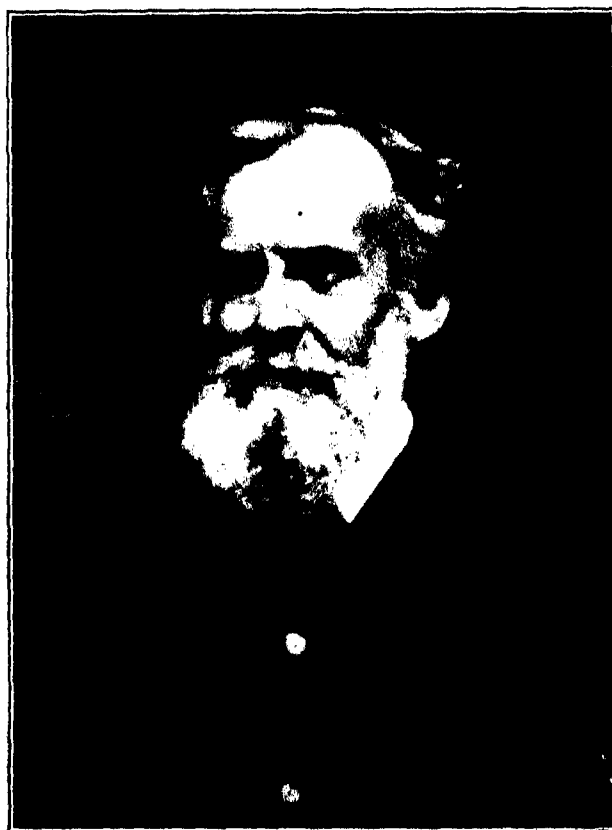
He was drawn to the study of logic by reading Mills, and in 1862, when he returned to Cambridge as Lecturer in Moral Science to his college, he became, with Sidgwick and Marshall, one of the principal lecturers on the subjects of the Moral Sciences Tripos. At this period Venn took a few private pupils, amongst them being Lord Balfour, Sir Charles Dilke, Professor Maitland, and Doughty, the traveller in Arabia.

In 1869 Venn delivered the Hulsean Lectures, his subject being the "Characteristics of Belief." In 1870 he relinquished Holy Orders. In 1903 he was elected President of his college and held that office until his death.

Venn's intellectual life falls into two distinct periods; in the first he was a student of logic, in the second an antiquary. He achieved distinction in both. The close of the first period is marked roughly by his election into our Society in 1883. The second period ended only with his death, for he was actively engaged on his great biographical history of the University of Cambridge to within a few days of that event.

His "Logic of Chance" was published in 1866, and later editions appeared in 1876 and 1888. It was, according to Dr. Keynes, "strikingly original and considerably influenced the development of the theory of statistics." "Probably his most enduring work on logic"—I quote again from Dr. Keynes—was the "Symbolic Logic," which appeared in 1881, with a second edition in 1894. "A great part of his treatment must always remain of value."

"The Principles of Empirical or Inductive Logic" appeared in 1889, in a second edition in 1907. "This followed on the general lines of Mills 'Logic,'



*John Venn*



and although it contained independent departures in many directions, it was less original than his other books."

That Venn should have become an antiquary was natural, since he was born in an antiquarian family and reared in traditional memories. His first important study in this direction was in the history of his own college [*Caius College (College Histories)*, 1901], and his second in the history of his own family ("*Annals of a Clerical Family*," 1904).

In 1886 he published the "*Admissions to Gonville and Caius College, 1558-1679*," and in 1897 "*The Biographical History of Gonville and Caius College, 1349-1897*." This great work, possibly the most detailed study of a social organisation ever made, would, if it stood alone, place Venn in the front rank of antiquaries, but it led to an even greater work, namely, a similar study of the University. This is the "*Alumni Cantabrigienses from earliest times to 1900*," (1922- ). In this immense work he was assisted by his son, and of it a brother antiquary writes :—"It is difficult for anyone who has not seen the work in its making to realise the immense amount of research involved in this great undertaking. Take, for instance, one section of the inquiries—a large one—that of the Clergy. In most dioceses Dr. Venn ransacked the Bishop's Registers and Act Books, the volumes of 'Subscriptions for Orders,' the Episcopal Visitations, the Book of Institutions and of First Fruits at the Record Office. From such details let the reader judge his methods of inquiry and research !"

All this research bore fruit other than the detailed records set out in the "*Alumna*," for Venn was keenly alive to the human and not infrequently humorous sides of his study. The result was not a few asides, always most interesting, on manners and people, which were published for the most part in the *Caius College Magazine*.

Venn had mechanical gifts out of the common, and was something of a craftsman. Later in his long life he turned this ability to curious use by devising and constructing a machine for bowling, the efficiency of which was demonstrated at Fenners on the occasion of the visit of the Australian Team to Cambridge in 1909, when the redoubtable Victor Trumper was clean bowled by it four times !

A good field botanist, a bit of a mountaineer, a craftsman, and with a gift of dry humour, Venn lived his long life to the full. Age treated him kindly—an active, spare man, he retained his sprightly walk and his interest in work and play until the end.

A personal note, to which the present writer is greatly indebted, was contributed by the late H. T. Francis to the *Caius College Magazine*.

W. B. H.

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## JOHN YOUNG BUCHANAN—1844-1925.

JOHN YOUNG BUCHANAN was born on February 20, 1844, the son of John Buchanan of Dowanhill. He was educated at Glasgow High School and University, and he subsequently studied at the Universities of Marburg, Leipsic and Bonn and at the École de Médecine, Paris. It was at these places that he acquired his unusual facility in German and French, and later he acquired a considerable knowledge of Spanish.

Buchanan was appointed chemist to the "Challenger" and took a leading part in the marine investigations carried out by the most completely equipped vessel that has ever circum-navigated the world. One of the most sensational discoveries thought to have been made by the expedition was that of *Bathypilus*, a glairy, viscid, granular substance which was constantly turning up in the jars containing the zoological specimens preserved in alcohol, collected by the zoologists. This was investigated by Huxley, who stood godfather to it. He regarded this as a form of primitive life which seemed to be spread all over the floor of the deep sea. It was Buchanan, however, who exploded the idea and showed that this substance was some kind of amorphous form of sulphate of lime precipitated by the addition of sea water to the alcohol in which marine organisms are preserved. It was characteristic of Huxley that he acknowledged his mistake and never mentioned the matter again. The chief contribution of Buchanan to the scientific results of H.M.S. "Challenger" was a section on the chemistry and physics of sea-water. He also contributed the narrative volumes and no doubt, after the death of Sir Wyville Thomson, he might have taken part in editing the volumes, but he preferred to devote himself to research.

The best known and probably the most important part of Buchanan's work was that carried out during the voyage of the "Challenger," and after the return in working out the results incorporated in the 'Report' of the voyage. He also published a large number of independent papers in various periodicals and in the journals of learned societies. Many of these scattered contributions have been brought together in two volumes, entitled respectively 'Comptes Rendus of Observation and Reasoning,' 1917, and 'Accounts Rendered of Work Done and Things Seen,' 1919. These cover a very wide range of subjects, not only chemical, physical and oceanographical, but geographical, zoological, astronomical, even accidents to ships, on railways, and to airships, testifying to a great range of knowledge and observation, as well as keenness of reasoning and inference. Besides all this, it is well known that Buchanan carried out, purely for his own satisfaction, a great amount of experimental work that was never published at all: when his own personal curiosity was satisfied he often let the subject drop, being quite without any desire for personal "kudos" or self-advertisement.



*J. G. Buchanan*





Perhaps the most remarkable features of Buchanan's varied work, were its thoroughness, its accuracy and the ingenuity displayed in the devising of methods and the construction of efficient apparatus, often out of the most homely materials. It should also be remembered that much of his experimental work was done out of doors, not only in tropical seas, but in the discomfort of the Antarctic and among the glaciers of the High Alps. All this adds very greatly to its value, as well as affording an instructive side-light on the man and his mental outlook.\*

Buchanan's family were comparatively wealthy. His mother, a most vigorous and radical old lady, had a fine house in Moray Place, Edinburgh. She was a very ardent Liberal and used to entertain Parnell and other advanced politicians. When they were there, Buchanan, who was an equally convinced Tory, was not.

His researches cover a wide field. From 1889 to 1903 he was lecturer in Geography at the University of Cambridge and, owing to his friendship with Prof. Robertson Smith he joined Christ's College, where he continued to reside in ample rooms for some 20 years. He was a brilliant talker, and when he left Cambridge the Combination Room of his College suffered a great loss. Owing to his intimate friendship with the late Prince of Monaco, the Duke Karl Theodor of Bavaria, and his acquaintance with the ex-Kaiser, he had unusual opportunities to observe the trend of European politics. He was convinced war was coming and he took the gloomiest views as to its outcome. So depressed was he that at the outbreak of war he went to Cuba and resided in Havana for the winter of 1914-15. Afterwards he took rooms in an hotel in Boston and remained there till the Armistice was declared. Before the war he had a comfortable house in Park Lane, but he sold all his possessions, and on returning to England lived in a couple of rooms in a West End hotel, though he occasionally went long voyages and spent some time in Glasgow. He had all the sailor's dislike for "gear," and long before he died he had reduced his worldly possessions to what could be held in a couple of trunks.

He was an extremely generous man and was always willing to help any deserving case of poverty, and he would give costly books and other objects to the College. He was always a very true and genuine friend. His fine presence and handsome face, tinged with melancholy, have been recorded in a picture now hanging in the Master's Lodge at Christ's College, by Louis Tinayre, brother of the well-known French novelist, Marcelle Tinayre. He was not a man who made friends very readily, and he certainly did not wear his heart on his sleeve. But once a friend you were always a friend, for he was a man whose quality of heart equalled the quality of his brain.

A. E. S.

\* For the two preceding paragraphs I am indebted to Dr. R. H. Rastall.

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## OLIVER HEAVISIDE—1850–1925.

OLIVER HEAVISIDE was born in London on May 13, 1850. He was a nephew of Sir Charles Wheatstone. After leaving school he was appointed to a post with the Great Northern Telegraph Company at Newcastle-on-Tyne. In 1874, in consequence of increasing deafness, he retired from business life and went to live in Devon. Between the years 1873 and 1892 he communicated a number of papers, some of great importance, to various societies and journals. Their value, however, was not at first recognised. In some respects his mathematical methods were novel; in consequence, he frequently had difficulty in getting his work published, and the rejection of some of it by the Society of Telegraph Engineers was for long a source of bitter grief.

In 1892 he collected these papers into two volumes; they became readily accessible, and the fact that the reader could study his investigations in a connected form led to a fuller appreciation of their value. His paper "On Duplex Telegraphy" (vol. i, p. 18) was originally published in the 'Philosophical Magazine' for June, 1873. In it he shows for the first time that quadruplex telegraphy is practicable, and considers it highly probable that multiplex telegraphy will come into everyday use. In 1881 he communicated a paper to the Society of Telegraph Engineers (now the Institution of Electrical Engineers) on the theory of the electrostatic and electromagnetic induction between parallel wires. This paper has recently come into importance in connection with the interference produced by induction between electric railway lines and telephone circuits.

Heaviside was the first (1884) to solve the problem of the high-frequency resistance and inductance of a concentric main. It was hardly known until Kelvin gave some of his results in his Presidential Address to the Institution of Electrical Engineers in 1889. In the two volumes of "Electrical Papers," Heaviside's most important practical work was laying the foundation of the modern theory of telephonic transmission, a theory which has proved of the utmost value to the telephonist. He points out that the difficulties which arise in telephony are due to the different attenuations and the different velocities of the various component waves which carry the necessary currents. His theory of the distortionless circuit (vol. ii, pp. 123–155) shows clearly the method on which long-distance telephony can be developed. Working on similar lines some ten years later, Professor Michael Pupin, in the United States, developed his loading coils (a method which Heaviside also invented) and long-distance telephony became practicable. Continuous loading of the cable was subsequently introduced, and Heaviside's simple theory became immediately applicable.

All his work proves conclusively the value of a knowledge of physics, and particularly of mathematical theory to the electrical industry. His methods of using a differential galvanometer and also of measuring mutual inductance are of great value in themselves. Like most of his work, also, they have been most fruitful in suggesting similar methods to others.

After the publication of 'Electrical Papers' in 1892, the importance of his work was recognised by electrical engineers. In the following year, 1893, the first volume of his 'Electromagnetic Theory' appeared, to be followed by a second in 1899. The third and concluding volume was published in 1912. The contents of this work are a sufficient indication of his contributions to electrical science.

Heaviside was the first to give the theory of the steady rectilinear motion of an electric charge through the ether, a theory which has been developed by others with important results. He was one of the first to predict the increase of mass of a moving charge when its speed becomes very great. In June, 1902, Heaviside wrote the article on the "Theory of the Electric Telegraph," in the 'Encyclopædia Britannica.' It is reprinted in 'Electromagnetic Theory,' vol. iii, p. 331. He gives a radiational theory founded on Maxwell's theory of light, and points out that experiment has verified all its essential points. Some of the theorems given in this article have been frequently quoted by the writers of text-books. In particular, his suggestion of a conducting layer in the upper atmosphere, by means of which electromagnetic waves are bent round the earth, is now well known and generally accepted.

He became a Fellow of the Royal Society in 1891; in 1908 he was elected an Honorary Member of the Institution of Electrical Engineers, and when the Faraday Medal of the Institution was founded in 1921, he was the first recipient. He died at Torquay on February 5, 1925.

A. R.

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## ANDREW GRAY—1847-1925.

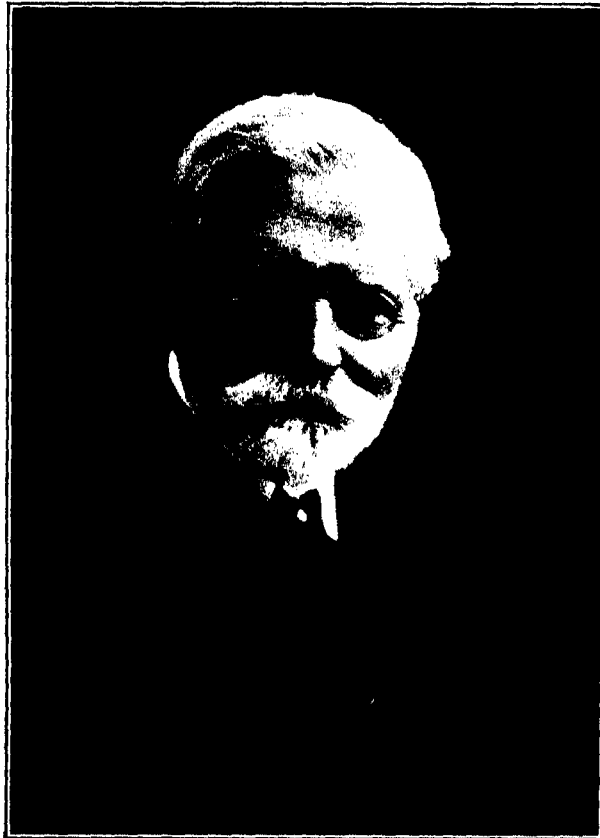
ANDREW GRAY was born at Lochgelly in Fifeshire in 1847. His education was the usual education of a Scottish boy who is the son of parents of limited means. The master at the village school he attended laid stress on the practical importance of mathematics, and taught the boys the elements of surveying. In particular, he showed them how to measure the distance of conspicuous objects out of doors by means of a measured base line. In this way Gray, when a boy, measured the distance of Nelson's monument on the Calton Hill, the lighthouse on the island of Inchkeith, the Martello tower at Leith Harbour, North Berwick Law, and other objects that can be seen from Burntisland. The practical nature of the teaching intensely interested the boys. In later life Gray always tried to make the problems he set the students as practical and as humanly interesting as possible.

At Glasgow University he gained many prizes and graduated M.A., with honours in Mathematics and Natural Philosophy.

His University distinctions, however, inadequately represented his attainments. On more than one occasion, when a student, he had to leave the University a few weeks before the end of the Session in order to assist in farming operations at home. In the opinion of Dr. Lushington, this once lost him the gold medal which is given to the best student in the Senior Greek class. Most students would have been grievously disappointed at losing eagerly coveted honours, but Gray ever put duty before personal ambition, and did not seem to mind. To the end of his life he remained an excellent classical scholar, and had a keen appreciation of Greek and Latin poetry. His Greek Testament was his constant companion, and in his letters he not infrequently made apt quotations from it. Like his friend, Professor Chrystal, he was an admirer of Schiller's poems, and knew many of them by heart.

From 1875-80 he was private secretary to Sir William Thomson, and from 1880-84 he was his official assistant. Thomson did not spare his assistants, and Gray had no easy task. About this time electrical engineering was making great strides, and Thomson had a devoted band of workers in his laboratory. Gray took a leading part in the testing of dynamos, at one time in conjunction with Dr. John Hopkinson, and in the testing of accumulators and of electric lamps.

In 1881-82 he attended Sir William Thomson's Senior Natural Philosophy Class. He corrected the examination papers of the class at the end of the term, and returned them to the students, of whom the writer was one. The writer found that not only had he written out the solutions of those questions



A. Gary.



which had been answered incorrectly, but he had also written out complete solutions of all those which he had not attempted. It must have taken him several hours, and shows the interest which he took in students and how he liked to help them.

In 1884 Gray was appointed to the Chair of Physics in the newly-founded University College of North Wales at Bangor. He had as colleagues two other old Glasgow students: Henry Jones, the distinguished philosopher, subsequently Sir Henry Jones, Professor of Moral Philosophy, and Gray's colleague at Glasgow University; and James J. Dobbie, afterwards Sir J. J. Dobbie, the Principal of the Government Laboratory. In 1896 he was made a Fellow of the Royal Society, and received the Hon. Degree of LL.D. from Glasgow University. While in Wales, he championed the cause of the higher education of women, and took a leading part in the foundation of the County School for Girls in Bangor. At this time he was also an enthusiastic mountaineer, and made weekly excursions with some of his colleagues into the Welsh hills. He was a strong swimmer, and rarely missed his morning bathe in the Menai Straits.

In 1899 he was installed Professor of Natural Philosophy at Glasgow University, a post which he resigned in 1924. During this period his strong personality, ability as a teacher and unwearying patience in explaining difficulties endeared his memory to many thousands of students. On the death of Lord Kelvin in 1907, Gray delivered an eloquent oration in his memory. He later expanded this into a book called 'The Scientific Work of Lord Kelvin.' It gives an excellent account of the life and activities of his famous predecessor.

Gray planned the present Natural Philosophy Institute of the University of Glasgow, a task which absorbed all his energies for several years. It was opened 18 years ago by the King and Queen, then Prince and Princess of Wales. He made special arrangements for the comfort of the students—in particular, the methods of ventilating and keeping at an equable temperature the large lecture rooms and laboratories are admirable. He also arranged an historical collection of Kelvin's apparatus in the Institute, but he felt that much of the interest of this collection would soon pass away, as the coming generation would not be able to picture the exciting times there had been when each improvement in the apparatus was perfected by Kelvin.

Gray wrote many books, published several addresses and communicated many papers to the Royal Societies of London and Edinburgh. His first book, entitled 'Absolute Measurements in Electricity and Magnetism,' was published in 1883. It deals almost exclusively with work of a fundamental character which was being carried out at that time by workers assisting Sir William Thomson. The first volume of an expansion of this work appeared in 1888 and a second volume in 1893. These works proved most helpful to physicists in National Laboratories when determining our electrical standards. In 1921



a final edition of 'Absolute Measurements' appeared. He once said that the writing of this book was difficult owing to—if not the discouraging—at least the Laodicean attitude of scientists to absolute measurements. In 1895 he published, in conjunction with George Ballard Mathews, a 'Treatise on Bessel Functions.' In this book practical applications are always kept in view. The treatise, which became a classic, was revised by Prof. Gray and Dr. T. M. MacRobert in 1922.

In 1898 appeared a treatise on 'Magnetism and Electricity,' and in 1901 a volume on 'Dynamics and Properties of Matter.' In 1911, in conjunction with his son, Prof. J. G. Gray, he published a treatise on 'Dynamics.' This book was written for students of physics and engineering, and contains a very large number of interesting examples, complete solutions of many of which are given. In 1919 appeared 'A Treatise on Gyrostatics and Rotational Motion.' This book is a monument to the vigour and industry of the author, as well as to his thorough knowledge of the subject.

In 1912 the writer had occasion to write to Gray to ascertain his opinion on the proposed use of the word "Kelvin" to denote the unit of electrical energy. In particular, he asked him what he thought Lord Kelvin's feeling would be likely to be if he were alive. He replied: "I have no hesitation in saying that I think the idea would not be distasteful to him, but the contrary. That view I base on my general reading of Lord Kelvin's character and disposition. He certainly did like recognition and appreciation (no blame to him for that!), and I am sure that any legitimate mode of perpetuating his name and fame which his colleague-workers in electrical science had insisted on inaugurating would have been gratefully received during his lifetime." Personally, however, Gray was strongly opposed to the giving of the names of eminent scientific men, *nomina clara et venerabilia*, as designations for practical electrical units. On another occasion, when criticising parts of 'Thomson and Tait' he wrote: "You will understand that I yield to no one in respect for the genius and memory of my great teacher and predecessor."

He was very interested in Einstein's Theory and had intended to give lectures on the subject. He thought it a pity that it was generally presented in the form of the "theory of tensors." In a letter written in 1923 he says: "Some of the conclusions of the Theory—e.g., as to the magnitude of the universe—are hardly translatable out of the non-Euclidean geometry without a dislocation of our reason. I cannot follow the conclusions . . . by the methods of common sense, if such methods be applicable. They almost seem to outrage all our old ideas." The Einsteinians were very sane people, but it was difficult to reconcile some of their results with sanity. "I don't know what to think."

Prof. Gray was very happy in his home life. He is survived by his widow, three sons and four daughters. There was an interesting family gathering when he and his wife celebrated their golden wedding five years ago. He was

glad when his second son James gave up engineering and followed in his footsteps—a decision which has since been justified by the excellent work he has done in gyrostatics and his appointment as Professor of Applied Physics in the University of Glasgow. In his later years he loved to spend his vacations in the Perthshire Highlands, where golden eagles are still to be seen. The remembrance of his happy, kindly and active life will be treasured by his many old pupils.

A. R.

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